Synthesis of Fluoroalkyl Methyl Thioethers by Formal Addition of Methanesulfenyl Fluoride to Alkenes

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Received May 21, 1991

The electrophilic anti-1,2-addition of the elements of methanesulfenyl fluoride to carbon–carbon double bonds by a one-pot reaction of dimethyl(methylthio)sulfonium tetrafluoroborate and triethylamine trishydrofluoride with various types of alkenes is used for the synthesis of β-fluoroalkyl methyl thioethers. This reaction is stereospecific: starting from *cis*-cycloalkenes (1) *trans*-1-fluoro-2-(methylthio)cycloalkanes (2) are formed, while *trans*-cyclododecene (3) gives the cis product 4 everytime in good yields. With unsymmetrical alkenes these reactions proceed regioselectively to produce Markovnikov-oriented fluoro thioethers. With 2,6-norbornadiene (26) exclusive exo attack on one double bond and subsequent transannular participation of the second π-bond gives rise to two isomeric 3,5-disubstituted nortricyclanes, 28 and 29, while starting from the medium-sized *cis,cis*-1,5-cyclooctadiene (10) no transannular π-participation is observed: the trans-1,2-addition product to one of the two double bonds in 11 is isolated. In contrast, in the reaction of the monoepoxide 30 of this diene in addition to the simple 1,2-adduct 31 a transannular oxygen participation occurs producing three oxa bicyclic compounds 32–34. The oxidation of 1-fluoro-2-(methylthio)cyclooctane (2a) by sodium periodate yields the expected mixture of two diastereomeric 1-fluoro-2-(methylsulfinyl)cyclooctanes (36) which on pyrolysis give 3-fluorocyclooctene (37).

Introduction

In recent years monofluorinated organic compounds have become interesting both from the synthetic[1] and biological[2] points of view. However, general methods for the mild and selective introduction of a single fluorine substituent into organic molecules are limited.[3] Usually special reagents, special equipment, and/or drastic conditions are required.[4] Around 1980 a new reagent, triethylamine trishydrofluoride ($Et_3N{\cdot}3HF$),[5] became commercially available, which we and others have shown to be a versatile source for fluoride anions in ring-opening reactions of epoxides,[6] aziridines,[7] and aziridinium ions,[8] as well as for the nucleophilic displacement of a triflate group by fluoride,[9] for halofluorination reactions,[10] and for selenofluorinations of unsaturated compounds.[11]

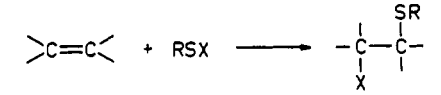
In a preliminary communication[12] we have reported the formal addition of methanesulfenyl fluoride to unsaturated substrates, by the reaction of alkenes with the combination of dimethyl(methylthio)sulfonium fluoroborate (DMTSF)[13] and $Et_3N{\cdot}3HF$.

The electrophilic addition of sulfenyl halides (mostly arene- or methanesulfenyl chlorides, sometimes bromides, but rarely iodides or fluorides) to alkenes yielding β-halo thioethers is a well-established reaction.[14,15]

In polar media the reactions are two-step processes involving the rate-determining initial formation of bridged episulfonium ions and their subsequent anti opening by halide ions.[14,15] However, under nonpolar conditions the absence of ionic intermediates and the intermediacy of a neutral sulfurane has been suggested, since solvent incorporation and skeletal rearrangements are not observed[16] and the reaction kinetics are insensitive to substituent groups of alkenes in benzenesulfenyl chloride addition.[17]

The direct addition of the elements of "normal" alkyl- or arylsulfenyl fluorides to alkenes forming β-fluoroalkyl thioethers has not been previously described. However, the addition of trifluoromethanesulfenyl fluoride to propene and (trifluoromethyl)ethylene was recently reported.[18] Known sulfenyl fluorides belong so far exclusively to the perfluorinated or perchlorofluorinated alkyl series. Trifluoromethanesulfenyl fluoride was synthesized,

Chart I



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(6) (a) Alvernhe G.; Laurent, A.; Haufe, G. *J. Fluorine Chem.* **1986**, *34*, 147. (b) Aranda, G.; Jullien, J.; Martin, J. A. *Bull. Soc. Chim. Fr.* **1965**, 1890. (c) Aranda, G.; Jullien, J.; Martin, J. A. *Ibid.* **1966**, 2850.

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(12) Preliminary report, Haufe, G.; Alvernhe, G.; Anker, D.; Laurent, A.; Saluzzo, C. *Tetrahedron Lett.* **1988**, *29*, 2311.

(13) (a) Meerwein, H.; Zenner, K. F.; Gipp, R. *Liebigs Ann. Chem.* **1965**, *688*, 67. (b) Smallcombe, S. H.; Caserio, M. C. *J. Am. Chem. Soc.* **1971**, *93*, 5826.

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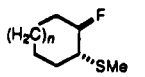
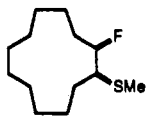
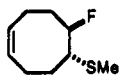
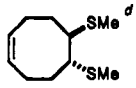
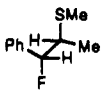
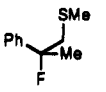
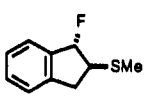
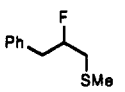
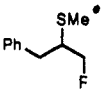
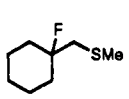
(18) Gombler, W.; Bollmann, G. *J. Fluorine Chem.* **1987**, *34*, 475.

0022-3263/92/1957-0714$03.00/0

Table I. Fluorosulfenylation Products of Alkenes (See Also Charts III–VI)

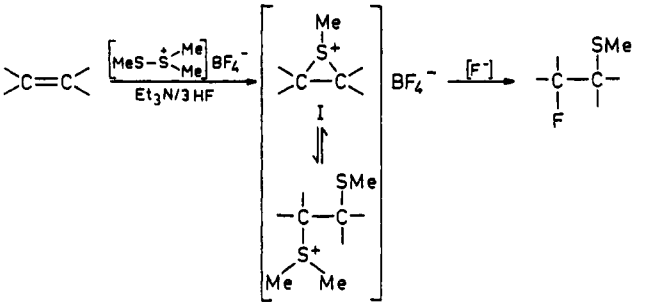
entry	alkene	β-fluoroalkyl methyl thioether		yield (%)	reaction time (h)
1	 1	 2	a: $n = 1$	90[a]	24
2			b: $n = 3$[b]	70[a]	48
3			c: $n = 7$	80[c]	48
4	 3	 4		90[c]	48
5	 10	 11 +  12		76[a]	48
6	 13	 14		90[a]	72
7	 15	 16		96[c]	17
8	 17	 18		90[c]	2
9	 19	 20 +  21		95[c]	4
10	 22	 23		90[c]	3

[a] After distillation. [b] Already known.[24,27] [c] After silica gel chromatography. [d] 7% of 12 is isolated which is already known.[33] [e] Ratio 56:44, determined by ^{19}F NMR spectroscopy. [f] Already known.[27]

but in fact, it is in equilibrium with its dimer.[15] Benzene- and methanesulfenyl fluorides itselves were previously only mentioned as unstable intermediates.[19]

However, β-fluoroalkyl phenyl thioethers have been already synthesized from bromo fluoro compounds by nucleophilic displacement of the bromo substituent by the phenylthio group.[20,21] Some other syntheses starting from β-halo thioethers by halogen-interchange reactions are known, but, when potassium fluoride was tried in different solvents, elimination predominated, although some cases were successful using silver fluoride.[22] Recently the preparation of 1-fluoro-2-(phenylthio)alkanes has been described by the reaction of alkenes with benzenesulfenyl chloride and silver fluoride in acetonitrile[23] or by ring opening of stabilized episulfonium ions with cesium fluoride[24] obtained in one or two steps from alkenes,[25] while Helmkamp et al. observed mainly elimination to form the olefin in the reaction of stabilized episulfonium ions with potassium fluoride.[26]

Chart II



II

Very recently we demonstrated that β-fluoroalkyl phenyl thioethers can be obtained by halogen exchange of β-chloroalkyl phenyl thioethers using triethylamine trishydrofluoride.[27]

On the other hand it has been reported that dimethyl(methylthio)sulfonium salts[28] can be directly added to alkenes to form episulfonium salts.[29] Furthermore,

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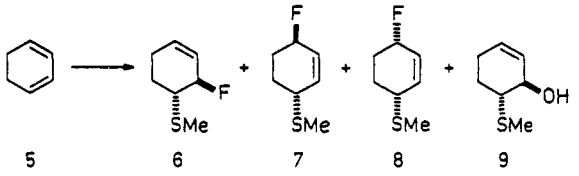
(28) For the structure and spectroscopic behavior of such salts, cf.: Minkwitz, R.; Prenzel, H.; Pritzkow, H. *Z. Naturforsch.* **1987**, *42b*, 750.

(29) Capozzi, G.; De Lucchi, O.; Lucchini, V.; Modena, G. *Tetrahedron Lett.* **1975**, 2603.

Chart III



5 6 7 8 9

these salts were opened in situ with various types of nucleophiles to form new carbon–sulfur,[30,31] carbon–nitrogen,[32] carbon–oxygen,[33,34] or carbon–carbon bonds,[33,34] respectively.

We report now a detailed study on the reaction of various olefins with dimethyl(methylthio)sulfonium fluoroborate (DMTSF) and triethylamine trishydrofluoride ($Et_3N{\cdot}3HF$).

Results and Discussion

The reactions of various types of olefins with DMTSF and $Et_3N{\cdot}3HF$ in methylene chloride at room temperature gave β-fluoroalkyl methyl thioethers in good yields[12] (Table I).

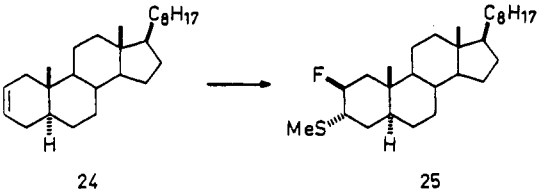
The products were isolated by distillation or column chromatography as indicated in Table I and identified by spectroscopic methods, mainly ^1H, ^{13}C, and ^{19}F NMR spectroscopy.

The addition of DMTSF to alkenes gives episulfonium ions I which can be formed also from methylbis(methylthio)sulfonium salts.[35] In the absence of stronger nucleophiles, ions I are perhaps in equilibrium with a sulfonium salt II. In the case of the reaction of cyclooctene and dimethyl(methylthio)sulfonium trinitrobenzenesulfonate such a salt has been isolated by Helmkamp et al.[30a] In the presence of $Et_3N{\cdot}3HF$ an irreversible displacement of dimethyl sulfide by fluoride ion, assisted by the methylthio group, occurs forming the desired β-fluoroalkyl methyl thioethers with retention of the configuration at the involved carbon atoms.

Starting from simple *cis*-cycloalkenes (Table I, entries 1–3) trans-1,2-disubstituted products are formed in accordance with other sulfenylation reactions.[14,36] For example *cis*-cyclododecene (**1c**) leads to *trans*-1-fluoro-2-(methylthio)cyclododecane (**2c**), while the reaction of *trans*-cyclododecene (**3**) yields *cis*-1-fluoro-2-(methylthio)cyclododecane (**4**) as the sole product. Thus the reaction is a stereospecific anti-1,2-addition.

With 1,3-cyclohexadiene (**5**) *trans*-3-fluoro-4-(methylthio)cyclohexene (**6**) was found as the sole fluorinated product after 40 min at 0 °C accompanied by 20% of **9** (^{13}C NMR); allylic rearrangement forming 1,4-products **7** and **8** is observed only as a minor process when the reaction is continued for 4 h at 20 °C. This lack of rearrangement is already known from other sulfenylation reactions of 1,3-dienes.[37] Additionally a consecutive product of **6**, alcohol **9**, was isolated which is formed during workup perhaps by a process similar to that described earlier by Carretero et al.[38]

Chart IV



24 25

The structural assignment for the main compound **6** which is formed by introduction of the fluoride into the allylic position was deduced mainly from ^{13}C NMR data. The doublet of carbon 3 appears at δ 90.7 ppm (J_{CF} = 169.1 Hz) and correlates with the proton signal at δ 4.93 ppm, which has a large coupling constant of $^2J_{HF}$ = 48.9 Hz which is characteristic of a geminal arrangement of the atoms. The strong downfield shift of this proton (compared to δ_H 4.4 ppm for the corresponding proton in the saturated analogue **2a**) indicates its allylic position. Moreover, the coupling constants $^2J_{CF}$ = 20.3 Hz or $^3J_{CF}$ = 9.6 Hz for the unsaturated carbons C-2 (δ 124.9 ppm) or C-1 (δ 132.5 ppm), respectively, rule out the other possible 1,2-regioisomer. On the other hand the large coupling constant of 19.2 Hz for the carbon atom bearing the methylthio group (δ 46.1 ppm) proves the 1,2-position of the substituents. In addition a second product was identified as *trans*-6-(methylthio)-2-cyclohexenol (**9**). The minor components **7** and **8** could not been isolated in pure form; however, the signals for the fluorine-bearing carbons appearing at δ 84.9 ppm ($^1J_{CF}$ = 164.9 Hz) and δ 84.0 ppm ($^1J_{CF}$ = 163.9 Hz) correlate as well to the proton doublet at 4.93 ppm. But the signals of the carbons bearing the methylthio group (δ 46.4, 46.1 ppm) are singlets, indicating that structures **7** and **8** are very probable.

cis,cis-1,5-Cyclooctadiene (**10**), a member of the medium-sized rings, by simple 1,2-addition yields *trans*-5-fluoro-6-(methylthio)cyclooctene (**11**) without participation of the second double bond (Table I, entry 5). Such π-participations (π-cyclizations), however, were obtained in several electrophilic additions toward this diene.[39] On the other hand the same simple pathway was found in other sulfenylation reactions[40] and other electrophilic additions involving strongly bridged intermediate cations as reaction intermediates.[41]

The reactions of unsymmetric olefins with DMTSF/$Et_3N{\cdot}3HF$ are regioselective Markovnikov-oriented additions. Starting from ethylenic compounds with benzylic positions (Table I, entries 6–8), only the products **14**, **16**, and **18**, respectively, were found having fluorine in that position (^{19}F NMR).

On the other hand, with allylbenzene (**19**) as the starting olefin the Markovnikov product **20** is formed in only a slight excess over the anti-Markovnikov-oriented compound **21** (Table I, entry 9). In this case neither steric nor electronic effects are important enough to direct the attack by fluoride strictly into one or the other position. In the bromofluorination of this olefin, however, the intermediary

(30) (a) Helmkamp, G. K.; Olsen, B. A.; Pettitt, D. J. *J. Org. Chem.* **1965**, *30*, 676. (b) Helmkamp, G. K.; Olsen, B. A.; Koskinen, J. R. *Ibid.* **1965**, *30*, 1623.

(31) Caserio, C. M.; Fisher, C. L.; Kim, J. K. *J. Org. Chem.* **1985**, *50*, 4390.

(32) (a) Trost, B. M.; Shibata, T. *J. Am. Chem. Soc.* **1982**, *104*, 3225. (b) Caserio, M. C.; Kim, J. K. *Ibid.* **1982**, *104*, 3231.

(33) Trost, B. M.; Shibata, T.; Martin, S. J. *J. Am. Chem. Soc.* **1982**, *104*, 3228.

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(35) Cappozzi, G. *Pure Appl. Chem.* **1987**, *59*, 989.

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(37) (a) Mueller, W. H.; Butler, P. E. *J. Org. Chem.* **1968**, *33*, 2642. (b) Schmid, G. H.; Yeroushalmi, S.; Garratt, D. G. *Ibid.* **1980**, *45*, 910. (c) Hopkins, P. B.; Fuchs, P. L. *Ibid.* **1978**, *43*, 1208. (d) Golding, B. T.; Pombo-Villar, E.; Samuel, C. J. *J. Chem. Soc., Chem. Commun.* **1985**, 1444.

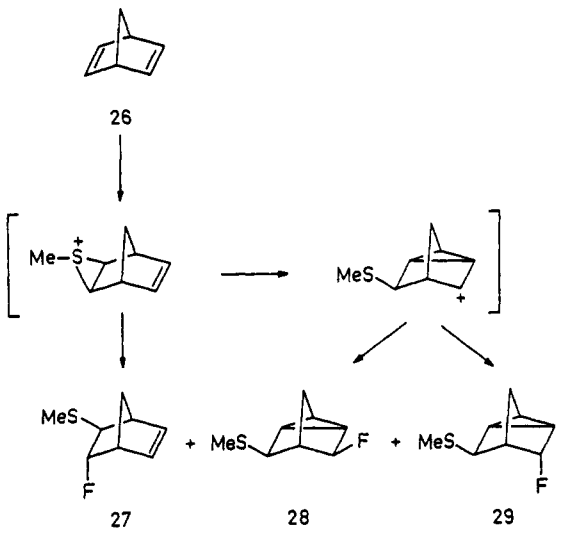
(38) Carretero, J. C.; Garcia Ruano, J. L.; Rodriguez; J. H. *Tetrahedron Lett.* **1987**, *28*, 4593.

(39) Haufe, G.; Mann, G. *Chemistry of Alicyclic Compounds—Structure and Chemical Transformations*; Elsevier: Amsterdam, 1989; p 373.

(40) (a) Trost, B. M.; Ochiai, M.; McDougal, P. G. *J. Am. Chem. Soc.* **1978**, *100*, 7103. (b) Schmid, G. H. *Can. J. Chem.* **1968**, *46*, 3757.

(41) (a) Haufe, G.; Alvernhe, G.; Laurent, A. *Tetrahedron Lett.* **1986**, *27*, 4449. (b) Labows, J. N.; Swern, D. *J. Org. Chem.* **1972**, *37*, 3004. (c) Fowler, F. W.; Hassner, A.; Levy, L. A. *J. Am. Chem. Soc.* **1967**, *89*, 2077.

Chart V



cation is less strongly bridged, and consequently the Markovnikov product dominates (89%) over the other regioisomer.[10a] With methylenecyclohexane (**22**) only the Markovnikov product **23** is formed without rearrangement of the starting olefin (Table I, entry 10).

Reaction of 2-cholestene (**24**), for 24 h gave only one isomer (**25**) in 96% yield bearing fluorine on carbon 2 and the sulfur function on carbon 3, both in axial position. Because of the steric hindrance caused by the methyl group at the C-10 position, the formation of the intermediate episulfonium ion in the α-position is favored, which is the normal process in addition reactions to this olefin, and has been already observed e.g. in epoxidation by peracids,[42] in bromination,[43] in iodoacetoxylation using iodine and silver acetate,[44] and in hydroxysulfenylation.[40] Several additional examples of additions to 2-cholestene or 2-androstene prove that the electrophilic attack takes place at the α-face.[45]

In contrast to all the above-mentioned reactions, in the case of 2,5-norbornadiene (**26**) only 5% (^{13}C NMR analysis) of the 1,2-addition product **27** was observed in the crude reaction mixture (5 h, 95%); two main isomers (73:27, ^{13}C NMR) were separated by column chromatography and identified to be *exo,exo*-2-fluoro-4-(methylthio)nortricyclane (**28**) and *endo*-2-fluoro-*exo*-4-(methylthio)nortricyclane (**29**) (exo and endo terms are used formally like in norbornane systems). These products are formed by exclusive exo attack of the electrophile on the double bond, followed by transannular π-participation in the intermediary bridged cation and final addition of fluoride to the nortricyclyl cation from the exo or endo side (cf. discussion in ref 11 for bromofluorination of this diene). This means that close proximity is necessary to have transannular participation of a π-bond.

To determine the effect of an oxygen function located in the transannular position relative to an intermediary cationic center, we performed the following reactions: By treatment of 9-oxabicyclo[6.1.0]non-4-ene (**30**) with DMTSF/Et_3N·3HF (8 h, 92% of crude product) mainly simple addition to the double bond yielding **31** (47%) but to some extent transannular participation of the epoxide ring (transannular O-heterocyclization[46]) also took place leading to compounds **32** (40%), **33** (7%), and **34** (6%) occurred (separated by column chromatography).

The structure of **31** is deduced mainly from ^{13}C NMR data, particularly from the ^{19}F–^{13}C coupling constants of fluorine at C-4 and carbons 1 and 8. Those couplings are only possible in a crown conformation **31A** where a *W* arrangement of fluorine an C-1 and C-8 gives rise to long-range coupling between C-1 (δ 55.6 ppm, $^4J_{CF}$ = 2.1 Hz) and C-8 (δ 55.1 ppm, $^5J_{CF}$ = 1.2 Hz). The structures of the other products follow from their spectroscopic data (cf. Experimental Section).

The electrophilic attack of DMTSF on **30** is possible from two directions leading to cis- or trans-oriented episulfonium ions III or IV, respectively, relative to the epoxide ring.

From cation III, however, no transannular participation of the oxygen function is possible. Consequently fluoride ion can enter from the opposite side to form **31**. On the other hand, in the intermediate IV transannular O-participation (O-heterocyclization) and subsequent incorporation of fluoride gives **32** and **33**, while dimethyl sulfide (which is always present in the reaction mixture) can compete with fluoride as a nucleophile, resulting in the formation of small amounts of **34**. The formation of **32**, **33**, and **34** must really occur by transannular attack of the epoxide ring on a cationic center formed from the double bond on the other side of the ring. The alternative possibility, i.e. first ring opening of the epoxide by Et_3N·3HF forming a fluorohydrin and then electrophilic attack and transannular participation of the OH group, is ruled out because the epoxide **30** does not react with this fluorinating agent at room temperature; even at 60 °C several hours are necessary to form **35**.[6a]

However, when using Olah's reagent (pyridine·9HF) instead of Et_3N·3HF, the reaction of **30** with DMTSF leads cleanly to compound **32** accompanied by only 6% of **33**. But also in this case the "intact" epoxide ring participates to form **32**, because **30** reacts with Olah's reagent to give π-participation products.[6a] On the other hand, **32** is formed as well from **35** and DMTSF in methylene chloride together with 8% of **33**.

A limiting factor for such "fluorosulfenylations" is the reactivity of the olefin. Using alkenes substituted with electron-withdrawing groups such as ethyl cinnamate or vinyl methyl sulfone the reaction fails. A similar failure has been observed also in the reaction of 3,4-didehydrosulfolane with benzeneselenenyl chloride in the presence of silver fluoride.[47]

The β-fluoroalkyl methyl thioethers formed by these reactions can be oxidized by known methods[48] to form the expected diastereomeric sulfoxides which, as already known from other sulfoxides,[49] eliminate methanesulfenic acid on heating to give allyl fluorides. In this way we succeeded in the preparation of a 3:2 mixture of the expected sulfoxides **36** from **2b** by treatment with sodium periodate.[50] The major diastereomer was separated by recrystallization from petroleum ether. However, both the pure isomer and the mixture of isomers gave 3-fluorocyclooctene (**37**) in 95% yield (^{19}F NMR, $C_6H_5CF_3$ as internal standard) on heating in cyclohexane for 20 h. Allyl fluorides are known to be unstable (cf. for example

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(50) Russell, G. A.; Ochrymowycz, L. A. *J. Org. Chem.* **1970**, *35*, 2106.

Chart VI

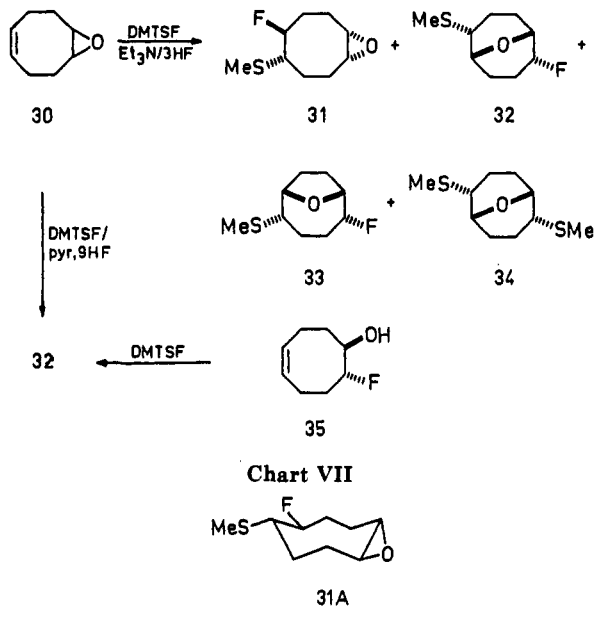

Chart VII

31A

ref 47) and **37** could not been distilled or isolated by column chromatography.

Experimental Section

Caution! Although triethylamine trishydrofluoride is less corrosive than Olah's reagent or anhydrous HF itself, any contact with the skin must be avoided. The reagents have been tested for laboratory use only. The experiments should be done under an efficient hood while wearing personal safety protection equipment.

General. ^{19}F NMR spectra were measured at 75.38 MHz in $CDCl_3$ and are reported in δ units (ppm) upfield from internal $CFCl_3$. Column chromatography was carried out on silica gel (Merck, 230–400 mesh) using petroleum ether (bp 45–65 °C) or petroleum ether/ether (9:1) as eluents.

Starting Materials. 2-Cholestene and *cis*- and *trans*-cyclododecene were prepared according to known procedures.[51,52] All other olefins are commercially available and were used without further purification. DMTSF has been prepared according to ref 13, and $Et_3N{\cdot}3HF$ is commercially available.

General Procedure. A solution of 10 mmol of the unsaturated compound in 20 mL of CH_2Cl_2 was treated at 0 °C with stirring with 11 mmol (2.16 g) of dimethyl(methylthio)sulfonium tetrafluoroborate (DMTSF). After 20 min, 50 mmol (8 mL) of triethylamine trishydrofluoride ($Et_3N{\cdot}3HF$) in 10 mL of CH_2Cl_2 was added dropwise at 0 °C, and stirring was continued for the time given in Table I. Then the reaction mixture was poured into ice–water, neutralized with dilute NH_3, and extracted 3× with 50-mL portions of ether. The combined ethereal extracts were washed with water and dried ($MgSO_4$). After evaporation of the solvent, the residue was purified by reduced-pressure distillation or column chromatography in some cases as indicated in Table I. However, all compounds were moisture-sensitive. Consequently in some cases impurities such as 2-(methylthio)cycloalkanols were found after hydrolytic workup or column chromatography.

***trans*-1-Fluoro-2-(methylthio)cyclohexane (2a)**: bp 78–79 °C (15 mmHg); ^1H NMR (300 MHz) δ 1.2–2.4 (8 H, m), 2.20 (3 H, s, SCH_3), 2.6–2.7 (1 H, m, H-2), 4.40 (1, H, ddd, d, $J_{H1,H2a}$ = $J_{H1,H6a}$ = 9.0 Hz, $J_{H1,H6e}$ = 4.1 Hz, J_{HF} = 48.6 Hz); ^{13}C NMR (75 MHz) δ 15.1 (q, d, $^4J_{CF}$ = 2.8 Hz, SCH_3), 23.1 (t, d, $^3J_{CF}$ = 9.3 Hz, C-5), 24.6 (t, d, $^4J_{CF}$ = 1.3 Hz, C-4), 30.3 (t, d, $^3J_{CF}$ = 5.2 Hz, C-3), 31.7 (t, d, $^2J_{CF}$ = 19.4 Hz, C-6), 49.2 (d, d, $^2J_{CF}$ = 18.2 Hz, C-2), 95.5 (d, d, $^1J_{CF}$ = 176.7 Hz, C-1); ^{19}F NMR ϕ = 170.0 (J_{FH} = 49 Hz).

***trans*-1-Fluoro-2-(methylthio)cyclooctane (2b)**: bp 72 °C (1 mmHg); (lit.[24] bp 80 °C, 2 mmHg); ^1H NMR (60 MHz) δ 1.1–2.1 (12 H, m), 2.18 (3 H, s, SCH_3), 2.5–3.2 (1 H, m, H-2), 4.58 (1 H, ddd, d, J_1 = 2.0 Hz, J_2 = 6.0 Hz, J_3 = 8.0 Hz, J_{HF} = 48.0 Hz); ^{13}C NMR (75 MHz) δ 15.5 (q, d, $^4J_{CF}$ = 3.9 Hz, SCH_3), 24.4 (t, d, $^3J_{CF}$ = 7.1 Hz, C-7), 25.4, 25.6, 26.2 (t, C-4, C-5, C-6), 28.5 (t, d, $^3J_{CF}$ = 7.0 Hz, C-3), 32.2 (t, d, $^2J_{CF}$ = 23.2 Hz, C-8), 50.5 (d, d, $^2J_{CF}$ = 21.5 Hz, C-2), 99.0 (d, d, $^1J_{CF}$ = 170.4 Hz, C-1); ^{19}F NMR ϕ 159.2 (J_{FH} = 48 Hz). Anal. Calcd for $C_9H_{17}FS$ (176.30): C, 61.31; H, 9.71; F, 10.78; S, 18.19. Found: C, 61.2; H, 9.8; F, 10.2; S, 18.8.

***trans*-1-Fluoro-2-(methylthio)cyclododecane (2c)**: liquid; ^1H NMR (60 MHz) δ 1.2–2.2 (20 H, m), 2.81 (1 H, m, d, $^3J_{HF}$ = 14.5 Hz, H-2), 4.76 (1 H, ddd, d, J_1 = 7.5 Hz, J_2 = 5.0 Hz, J_{HF} = 48.5 Hz); ^{13}C NMR (50 MHz) δ 15.3 (q, d, $^4J_{CF}$ = 6.9 Hz, SCH_3), 29.5 (t, d, $^2J_{CF}$ = 18.0 Hz, C-12), 20.1 (t, d, $^3J_{CF}$ = 4.7 Hz, C-11), 22.1, 23.2, 23.3, 23.4, 23.6, 23.9, 24.1 (t, C-4, C-5, C-6, C-7, C-8, C-9, C-10), 28.2 (t, d, $^3J_{CF}$ = 4.4 Hz, C-3), 47.1 (d, d, $^2J_{CF}$ = 18.3 Hz, C-2), 95.3 (d, d, $^1J_{CF}$ = 171.6 Hz, C-1); ^{19}F NMR ϕ 183.7 (J_{FH} = 49 Hz).

***cis*-1-Fluoro-2-(methylthio)cyclododecane (4)**: liquid; ^1H NMR (60 MHz) δ 1.2–2.2 (20 H, m), 2.80 (1 H, m, d, $^3J_{HF}$ = 25.5 Hz), 4.88 (1 H, ddd, d, J_1 = 6.0 Hz, J_2 = 1.5 Hz, $^3J_{HF}$ = 48.0 Hz); ^{13}C NMR (50 MHz) δ 14.6 (q, d, $^4J_{CF}$ = 2.7 Hz, SCH_3), 27.5 (t, d, $^2J_{CF}$ = 21.3 Hz, C-12), 21.2 (t, d, $^3J_{CF}$ = 4.7 Hz, C-11), 21.7, 22.0 (2 C), 23.2 (t, d, $^3J_{CF}$ = 2.7 Hz, C-3), 23.2, 23.7, 24.4 (t, C-4, C-5, C-6, C-7, C-8, C-9, C-10), 47.1 (d, d, $^2J_{CF}$ = 18.9 Hz, C-2), 95.3 (d, d, $^1J_{CF}$ = 173.9, C-1); ^{19}F NMR ϕ 183.1 (J_{FH} = 48 Hz).

***trans*-3-Fluoro-4-(methylthio)cyclohex-1-ene (6)**: liquid (purified by column chromatography); ^1H NMR (300 MHz) δ 1.4–2.2 (4 H, m), 2.20 (3 H, d, $^5J_{HF}$ = 0.8 Hz, SCH_3), 2.95 (1 H, ddd, d, J_1 = 3.3 Hz, J_2 = 6.3 Hz, J_3 = 9.6 Hz, $^3J_{HF}$ = 13.5 Hz, H-4), 4.93 (1 H, m, d, $^1J_{HF}$ = 48.9 Hz, H-3), 5.7–5.8 (1 H, m), 5.9–6.0 (1 H, m); ^{13}C NMR (75 Mz) δ 14.6 (q, d, $^4J_{CF}$ = 1.6 Hz, SCH_3), 24.0 (t, d, $^4J_{CF}$ = 3.1 Hz, C-5), 25.4 (t, d, $^3J_{CF}$ = 3.6 Hz, C-6), 46.1 (d, $^2J_{CF}$ = 19.2 Hz, C-4), 90.7 (d, $^1J_{CF}$ = 169.1 Hz, C-3), 124.9 (d, $^2J_{CF}$ = 20.3 Hz, C-2), 132.5 (d, $^3J_{CF}$ = 9.6 Hz, C-1); ^{19}F NMR ϕ 165.3 (J_{FH} = 49 Hz).

***trans*-3-Fluoro-6-(methylthio)cyclohex-1-ene (7)**: ^{13}C NMR (75 MHz) (determined in the mixture with **6** and **9**) δ 14.4 (s, SCH_3), 24.2 (d, $^3J_{CF}$ = 3.6 Hz, C-5), 26.9 (d, $^2J_{CF}$ = 19.8 Hz, C-4), 46.4 (s, C-6), 84.9 (d, $^1J_{CF}$ = 164.9 Hz, C-3), 127.3 (d, $^2J_{CF}$ = 19.7 Hz, C-2), 133.4 (d, $^3J_{CF}$ = 10.0 Hz, C-1); ^{19}F NMR ϕ 168.8.

***trans*-3-Hydroxy-4-(methylthio)cyclohex-1-ene (9)**: ^{13}C NMR (75 MHz) (determined in the mixture with **6** and **7**) δ 12.6 (s, SCH_3), 25.0, 26.8 (C-5 and C-6), 49.7 (C-4), 69.2 (C-3), 128.8, 129.1 (C-1 and C-2).

***trans*-5-Fluoro-6-(methylthio)cyclooct-1-ene (11)**: bp 54 °C (0.1 mmHg); ^1H NMR (60 MHz) δ 1.5–2.6 (8 H, m), 2.15 (3 H, s, SCH_3), 2.98 (1 H, m, d, $^3J_{HF}$ = 11.0 Hz), 4.63 (1 H, m, d, J_{HF} = 48.5 Hz), 5.2–5.9 (2 H, m); ^{13}C NMR (50 Mz) δ 15.7 (q, d, $^4J_{CF}$ = 5.3 Hz, SCH_3), 23.3 (t, d, $^3J_{CF}$ = 6.8 Hz, C-7), 24.4 (t, C-8), 30.6 (t, d, $^3J_{CF}$ = 5.7 Hz, C-3), 32.8 (t, d, $^2J_{CF}$ = 24.0, C-4), 48.7 (d, d, $^2J_{CF}$ = 19.8, C-6), 96.7 (d, d, $^1J_{CF}$ = 171.1, C-5), 127.4, 130.4 (d, C-1 and C-2); ^{19}F NMR ϕ 166.1 (J_{FH} = 49.0).

***trans*-5,6-Bis(methylthio)cyclooct-1-ene (12)**:[32] ^1H NMR (60 MHz) δ 1.2–2.5 (8 H, m), 2.10 (6 H, s, SCH_3), 2.98 (2 H, m, H-5, H-6), 5.68 (2 H, m, H-1, H-2); ^{13}C NMR (25 MHz) δ 16.2 (q, SCH_3), 24.7 (t, C-3, C-8), 33.6 (t, C-4, C-7), 51.3 (d, C-5, C-6), 129.9 (d, C-1, C-2).

***erythro*-1-Fluoro-1-phenyl-2-(methylthio)propane (14)**: bp 100 °C (0.1 mmHg); ^1H NMR (60 MHz) δ = 1.26 (3 H, s, d, J = 6.5 Hz), 1.80 (3 H, s, SCH_3), 2.4–3.2 (1 H, m), 5.35 (d, d, J = 6.5 Hz, J_{HF} = 47.0 Hz), 7.0–7.5 (5 H, m); ^{19}F NMR ϕ 176.8 (J_{FH} = 47 Hz). Anal. Calcd for $C_{10}H_{13}FS$ (184.28): C, 65.18; H, 7.11; F, 10.31; S, 17.40. Found: C, 65.4; H, 7.1; F, 9.9; S, 16.9.

2-Fluoro-1-(methylthio)-2-phenylpropane (16): liquid; ^1H NMR (60 MHz) δ 1.80 (3 H, d, $^3J_{HF}$ = 24.0 Hz), 1.95 (3 H, s, SCH_3), 2.95 (2 H, d, $^3J_{HF}$ = 20.0 Hz), 7.2–7.5 (5 H, m); ^{19}F NMR ϕ 144.9.

***trans*-1-Fluoro-2-(methylthio)indan (18)**: liquid; ^1H NMR (80 MHz) δ 2.20 (3 H, s, SCH_3), 2.5–3.2 (1 H, m), 3.2–3.9 (2 H, m), 5.82 (1 H, d, d, J = 4.0 Hz, J_{HF} = 57 Hz), 7.0–7.5 (4 H, m); ^{13}C NMR (75 MHz) δ 14.2 (q, SCH_3), 36.6 (t, C-3), 49.7 (d, d, $^2J_{CF}$ = 22.1 Hz, C-2), 101.2 (d, d, $^1J_{CF}$ = 182.2 Hz, C-1), 124.3 (d, d, J_{CF} = 1.6 Hz), 124.9 (d, d, J_{CF} = 1.4 Hz), 126.8 (d, d, J_{CF} = 2.7 Hz), 129.4 (d, d, J_{CF} = 3.4 Hz), (C-4, C-5, C-6, C-7), 138.5 (d, $^2J_{CF}$ = 17.4 Hz, C-8), 141.5 (d, $^3J_{CF}$ = 5.1 Hz, C-9); ^{19}F NMR ϕ 160.2.

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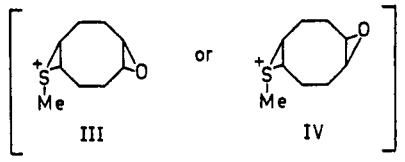
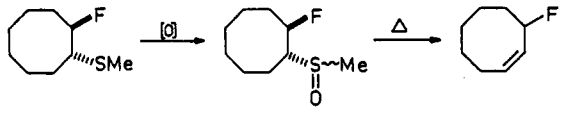
(52) (a) Nozaki, H.; Noyori, R. *J. Org. Chem.* **1965**, *30*, 1652. (b) Nozaki, H.; Nishikawa, Y.; Kawanisi, M.; Noyori, R. *Tetrahedron* **1967**, *23*, 2173.

Chart VIII



III IV

Chart IX



2b 36 37

2-Fluoro-1-(methylthio)-3-phenylpropane (20): liquid; ^{1}H NMR (60 MHz) δ 2.15 (3 H, s, SCH_3), 2.55 (2 H, d, d, J = 6.0 Hz, $^3J_{HF}$ = 21.0 Hz, H-3), 2.97 (2 H, d, d, J = 6.0 Hz, $^3J_{HF}$ = 21.0 Hz, H-1), 4.82 (1 H, dddd, d, $J_1 = J_2$ = 6.0 Hz, J_{HF} = 48.0 Hz, H-2), 7.31 (5 H, m); ^{19}F NMR ϕ 175.7 (J_{FH} = 47.5 Hz).

1-Fluoro-2-(methylthio)-3-phenylpropane (21): not separated in pure form (spectra were taken from the mixture of **20** and **21**); only one significant difference was determined for **21** in the ^{1}H NMR (60 MHz) spectrum δ 4.37 (1 H, d, d, J = 6.0 Hz, J_{HF} = 47.0 Hz); ^{19}F NMR ϕ 216.8 (J_{FH} = 47 Hz).

1-Fluoro-1-[(methylthio)methyl]cyclohexane (23):[27] bp 72–73 °C (15 mmHg); ^{1}H NMR (300 MHz) δ 1.2–2.1 (10 H, m), 2.16 (3 H, d, $^5J_{HF}$ = 1.0 Hz, SCH_3), 2.68 (2 H, d, $^3J_{HF}$ = 19.8 Hz, CH_2S); ^{13}C NMR (75 MHz) δ 17.7 (q, d, $^4J_{CF}$ = 2.7 Hz, SCH_3), 21.9 (t, d, $^3J_{CF}$ = 3.0 Hz, C-3, C-5), 25.3 (t, C-4), 34.5 (t, d, $^3J_{CF}$ = 22.2 Hz, C-2, C-6), 44.3 (t, d, $^2J_{CF}$ = 24.9 Hz, CH_2S), 96.2 (d, $^1J_{CF}$ = 173.1 Hz, C-1); ^{19}F NMR ϕ 153.4.

2β-Fluoro-3α-(methylthio)-5α-cholestane (25): mp 105–107 °C; ^{1}H NMR (60 MHz) δ 0.6–2.1 (44 H, m), 2.14 (3 H, s, SCH_3), 3.05 (1 H, m, d, J_{HF} = 14.0 Hz, H-3), 4.75 (1 H, m, d, J_{HF} = 48 Hz); ^{13}C NMR (75 MHz) δ 13.7 (q, d, $^4J_{CF}$ = 5.3 Hz, SCH_3), 28.2 (t, d, $^3J_{CF}$ = 2.3 Hz, C-4), 35.7 (d, $^3J_{CF}$ = 1.2 Hz, C-10), 38.3 (t, d, $^2J_{CF}$ = 18.4 Hz, C-1), 47.1 (d, d, $^2J_{CF}$ = 23.4 Hz, C-3), 92.0 (d, d, $^1J_{CF}$ = 176.0 Hz, C-2), 12.1, 15.9, 18.7, 20.9, 22.6, 22.8, 23.9, 24.1, 28.0, 28.2, 29.5, 31.7, 34.9, 35.8, 36.2, 39.5, 40.0, 40.8, 42.6, 54.7, 56.3, 56.4 (all other C atoms); ^{19}F NMR ϕ 163.8 (J_{FH} = 48 Hz).

***endo*-4-Fluoro-*exo*-5-(methylthio)norbornene (27)**: not isolated in pure form, ^{13}C NMR (50 MHz) (taken from an enriched sample of **27** in **29**) δ 15.8 (q, SCH_3), 44.9 (d, C-6), 46.7 (t, d, $^3J_{CF}$ = 2.1 Hz, C-7), 48.6 (d, d, $^2J_{CF}$ = 20.6 Hz, C-3), 54.2 (d, d, $^2J_{CF}$ = 22.6 Hz, C-5), 132.4 (d, d, $^3J_{CF}$ = 10.0 Hz, C-2), 139.4 (d, C-1); ^{19}F NMR ϕ 171.6.

***exo*-3-Fluoro-*exo*-5-(methylthio)tricyclo[2.2.1.0^{2,6}]heptane (28)**: liquid; ^{1}H NMR (60 MHz) δ 1.0–2.3 (6 H, m), 2.08 (3 H, s, SCH_3), 2.98 (1 H, s, H-5), 4.64 (1 H, d, J_{HF} = 60.0 Hz, H-3); ^{13}C NMR (50 MHz) δ 12.2 (q, SCH_3), 14.9 (d, C-1), 17.2 (d, d, $^2J_{CF}$ = 23.8 Hz, C-2), 19.5 (d, d, $^3J_{CF}$ = 6.1 Hz, C-6), 27.2 (t, C-7), 38.6 (d, d, $^2J_{CF}$ = 14.1 Hz, C-4), 48.1 (d, d, $^3J_{CF}$ = 3.3 Hz, C-5), 96.4 (d, d, $^1J_{CF}$ = 192.7 Hz, C-3); ^{19}F NMR ϕ 193.1 (J_{FH} = 59.5 Hz).

***endo*-3-Fluoro-*exo*-5-(methylthio)tricyclo[2.2.1.0^{2,6}]heptane (29)**: liquid; ^{1}H NMR (60 MHz) δ 1.0–2.7 (6 H, m), 2.05 (3 H, s, SCH_3), 3.30 (1 H, s, H-5), 4.79 (1 H, d, J_{HF} = 60.0 Hz, H-3); ^{13}C NMR (50 MHz) δ 15.0 (d, d, $^3J_{CF}$ = 6.9 Hz, C-1), 15.1 (q, SCH_3), 16.9 (d, d, $^2J_{CF}$ = 23.0 Hz, C-2), 17.1 (d, C-6), 26.6 (t, d, $^3J_{CF}$ = 3.5 Hz, C-7), 38.9 (d, d, $^2J_{CF}$ = 15.7 Hz, C-4), 49.8 (d, C-5), 98.7 (d, d, $^1J_{CF}$ = 188.7, C-3); ^{19}F NMR ϕ 199.0 (J_{FH} = 59.5 Hz).

***anti*-4-Fluoro-*syn*-5-(methylthio)-9-oxabicyclo[6.1.0]nonane (31)**: liquid; ^{1}H NMR (300 MHz) δ 1.38–1.53 (2 H, m, 2 H-3), 1.65–2.15 (6 H, m), 2.06 (3 H, s, SCH_3), 2.91 (2 H, m, H-1, H-8), 3.21 (1 H, m, H-5), 4.80 (1 H, ddd, d, J_1 = 3.7 Hz, J_2 = 4.4 Hz, J_3 = 8.4 Hz, J_{HF} = 46.1 Hz, H-4); ^{13}C NMR (75 MHz) δ 17.7 (s, d, $^4J_{CF}$ = 2.2 Hz, SCH_3), 23.2 (t, C-7), 23.6 (t, d, $^3J_{CF}$ = 2.0 Hz, C-6), 24.6 (t, d, $^3J_{CF}$ = 5.1 Hz, C-2), 29.1 (t, d, $^2J_{CF}$ = 22.2 Hz, C-3), 48.7 (d, d, $^2J_{CF}$ = 21.7 Hz, C-5), 55.1 (d, d, $^5J_{CF}$ = 1.2 Hz, C-8), 55.6 (d, d, $^4J_{CF}$ = 2.1 Hz, C-1), 93.2 (d, d, $^1J_{CF}$ = 177.1 Hz, C-4); ^{19}F NMR ϕ 167.8 (J_{FH} = 46 Hz).

***endo*-2-Fluoro-*endo*-6-(methylthio)-9-oxabicyclo[3.3.1]nonane (32)**: liquid; ^{1}H NMR (300 MHz) δ 1.75–2.35 (8 H, m), 2.11 (3 H, s, SCH_3), 3.06 (1 H, m, J_1 = 4.8 Hz, J_2 = 5.3 Hz, J_3 = 12.6 Hz, H-6), 3.87 (1 H, m, H-1), 4.01 (1 H, t, H-5), 4.87 (1 H, m, d, J_{HF} = 48.0 Hz, H-2); ^{13}C NMR (75 MHz) δ 14.2 (q, SCH_3), 23.1 (t, d, $^3J_{CF}$ = 8.8 Hz, C-4), 23.2 (t, C-8), 26.35 (t, d, $^2J_{CF}$ = 19.3 Hz, C-3), 26.4 (t, C-7), 46.0 (d, C-6), 67.3 (d, d, $^2J_{CF}$ = 24.3 Hz, C-1), 68.5 (d, d, $^4J_{CF}$ = 1.0 Hz, C-5), 88.9 (d, d, $^1J_{CF}$ = 178.6 Hz, C-2); ^{19}F NMR ϕ 182.6 (J_{FH} = 48 Hz).

***endo*-2-Fluoro-*endo*-5-(methylthio)-9-oxabicyclo[4.2.1]nonane (33)**: ^{1}H NMR (300 MHz) δ 1.70–2.30 (8 H, m), 2.16 (3 H, s, SCH_3), 2.88 (1 H, m, H-5), 4.57 (2 H, m, H-1, H-6), 4.92 (1 H, m, d, J_{HF} = 48 Hz, H-2); ^{13}C NMR (75 MHz) δ 15.1 (q, SCH_3), 24.9 (t, d, $^3J_{CF}$ = 3.4 Hz, C-8), 25.5 (t, C-7), 25.6 (t, d, $^3J_{CF}$ = 7.3 Hz, C-4), 30.0 (t, d, $^2J_{CF}$ = 21.6 Hz, C-3), 50.9 (d, C-5), 78.2 (d, d, $^2J_{CF}$ = 26.2 Hz, C-1), 81.5 (d, C-6), 92.2 (d, d, $^1J_{CF}$ = 176.0 Hz, C-2); ^{19}F NMR ϕ 183.7.

***endo,endo*-2,6-Bis(methylthio)-9-oxabicyclo[3.3.1]nonane (34)**: ^{1}H NMR (300 MHz) δ 1.60–2.30 (8 H, m), 2.10 (6 H, s, SCH_3), 2.97 (2 H, m, H-1, H-5); ^{13}C NMR (75 MHz) δ 14.2 (q, SCH_3), 23.6 (t, C-3, C-7), 26.8 (t, C-4, C-8), 46.3 (d, C-2, C-6), 68.6 (d, C-1, C-5).

***trans*-1-Fluoro-2-(methylsulfinyl)cyclooctane (36).** At 25 °C a solution of 3.52 g (20 mmol) of **2b** in 25 mL of acetonitrile was treated with stirring with a solution of 4.71 g (22 mmol) $NaIO_4$ in 25 mL of water. Stirring was continued for 18 h at rt. The mixture was filtered, and the filtrate was extracted three times with 25 mL of $CHCl_3$. After drying ($MgSO_4$), the solvent was evaporated, giving a 65:35 mixture of the two isomers of **36** as colorless crystals, mp 88–96 °C. The major diastereoisomer **36a** is separated by several crystallizations from petroleum ether: mp 91–93 °C; ^{1}H NMR (60 MHz) δ 1.3–2.0 (10 H, m), 2.20 (2 H, m, 2 H-3), 2.58 (3 H, s, $SOCH_3$), 2.80 (1 H, m, H-2), 4.90 (1 H, m, d, J_{CF} = 49.0 Hz, H-1); ^{13}C NMR (25 MHz) δ 20.1 (t, d, $^3J_{CF}$ = 7.1 Hz, C-3), 22.0 (t, d, $^3J_{CF}$ = 5.8 Hz, C-7), 25.3, 26.4, 27.6 (t, C-4, C-5, C-6), 30.8 (t, d, $^2J_{CF}$ = 22.3 Hz, C-8), 37.6 (q, d, $^4J_{CF}$ = 4.5 Hz, $SOCH_3$), 65.3 (d, d, $^2J_{CF}$ = 18.8 Hz, C-2), 91.9 (d, d, $^1J_{CF}$ = 170.4 Hz, C-1); ^{19}F NMR ϕ 169.4 (J_{FH} = 49 Hz). Anal. Calcd for $C_9H_{17}FOS$ (192.30): C, 56.21; H, 8.91; F, 9.88; S, 16.67. Found: C, 55.9; H, 8.8; F, 9.5; S, 16.6.

The minor isomer **36b** was not separated in pure form; the spectroscopic data were taken from the mixture of isomers. In the ^{1}H NMR spectrum only the signal of the $SOCH_3$ group is shifted to δ 2.53 ppm: ^{13}C NMR (25 MHz) δ 22.3 (t, d, $^3J_{CF}$ = 6.3 Hz, C-7), 22.8 (t, d, $^3J_{CF}$ = 7.4 Hz, C-3), 25.0, 26.3, 27.6 (t, C-4, C-5, C-6), 30.8 (t, d, $^2J_{CF}$ = 18.2 Hz, C-2), 34.6 (q, d, $^4J_{CF}$ = 4.8 Hz, $SOCH_3$), 62.4 (d, d, $^2J_{CF}$ = 19.5 Hz, C-2), 90.3 (d, d, $^1J_{CF}$ = 169.3 Hz, C-1); ^{19}F NMR ϕ 168.7.

3-Fluorocyclooct-1-ene (37). A suspension of 0.35 g (1.82 mmol) of pure **36a** or of the mixture of **36a** and **36b** in 3.5 mL of cyclohexane was heated for 20 h at 80 °C in a closed flask in the presence of trifluorobenzene as internal standard giving 95% (^{19}F NMR) of **37**: ^{1}H NMR (60 MHz) δ 1.3–1.7 (8 H, m), 1.8–2.3 (2 H, m, 2 H-4), 5.35 (1 H, m, d, J_{HF} = 45.0 Hz, H-3), 5.4–5.8 (2 H, m, H-1, H-2); ^{13}C NMR (75 MHz) δ 23.2 (t, d, $^3J_{CF}$ = 12.9 Hz, C-5), 26.2, 26.5, 29.3 (t, C-6, C-7, C-8), 36.8 (t, d, $^2J_{CF}$ = 22.8 Hz, C-4), 90.7 (d, d, $^1J_{CF}$ = 164.1 Hz, C-1), 128.4 (d, d, $^3J_{CF}$ = 12.9 Hz, C-1), 133.2 (d, d, $^2J_{CF}$ = 29.2 Hz, C-2); ^{19}F NMR ϕ 173.4 (J_{FH} = 45 Hz).

Acknowledgment. Financial support by CNRS to G.H. is gratefully acknowledged.

Registry No. 1 (n = 1), 110-83-8; 1 (n = 3), 931-88-4; 1 (n = 7), 1129-89-1; **2a**, 122895-30-1; **2b**, 75825-93-3; **2c**, 122895-31-2; **3**, 1486-75-5; **4**, 122923-50-6; **5**, 592-57-4; **6**, 137742-50-8; **7**, 137742-51-9; **8**, 137742-59-7; **9**, 137742-52-0; **10**, 111-78-4; **11**, 122895-32-3; **12**, 137742-53-1; **13**, 873-66-5; **14**, 122895-33-4; **15**, 98-83-9; **16**, 122895-34-5; **17**, 95-13-6; **18**, 122895-38-9; **19**, 300-57-2; **20**, 122895-35-6; **21**, 122895-36-7; **22**, 1192-37-6; **23**, 129110-65-2; **24**, 15910-23-3; **25**, 122910-83-2; **26**, 121-46-0; **27**, 137742-54-2; **28**, 122895-37-8; **29**, 122923-51-7; **30**, 637-90-1; **31**, 137742-55-3; **32**, 130516-72-2; **33**, 130516-73-3; **34**, 137742-56-4; **36** (isomer 1), 137821-41-1; **36** (isomer 2), 137742-58-6; **37**, 137742-57-5; DMTSF, 5799-67-7; $Et_3N{\cdot}3HF$, 73602-61-6; methanesulfenyl fluoride, 61671-43-0.

Supplementary Material Available: ^{1}H, ^{13}C, and ^{19}F NMR spectra for fluoroalkyl methyl thioethers (74 pages). Ordering information is given on any current masthead page.