

**FORMAL ADDITION OF METHANESULFENYL FLUORIDE
TO UNSATURATED SUBSTRATES**

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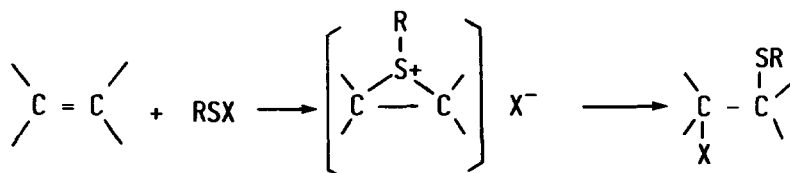
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Summary: The electrophilic *anti*-addition of the elements of methanesulfonyl fluoride towards carbon-carbon double bonds by a one pot reaction of dimethyl(methylthio)sulfonium fluoroborate and triethylamine tris-hydrofluoride with various types of alkenes is used for the synthesis of β -fluoroalkyl-methylthioethers.

The electrophilic addition of sulfonyl halides to alkenes leading to β -halothioethers is a very well-established two-step reaction involving the rate determining initial formation of bridged episulfonium ions and their subsequent *anti*-opening by halide ions^{1,2}.



The carbon residue R is usually an alkyl or aryl group and X is mostly chlorine, sometimes bromine, but rarely fluorine or iodine. The most commonly-used are arenesulfonyl chlorides or methanesulfonyl chloride^{1,2}.

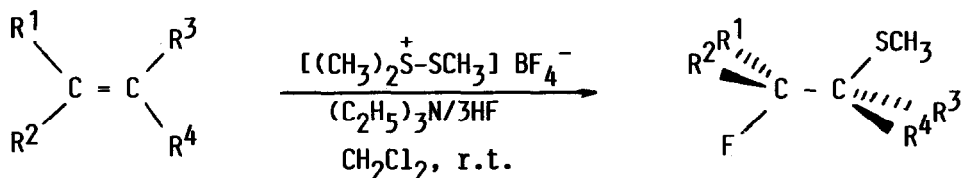
The direct addition of the elements of sulfonyl fluorides to alkenes forming β -fluoroethers has not yet been reported. The synthesis of such compounds starting from other β -halothioethers by halogen-interchange reactions is difficult because of the strong basic character of the fluoride anion favouring the elimination products when using KF

as the reagent³, but was, however, successful in some cases using AgF^4 . A second possibility was opened by Smit et al.⁵ by ring opening with CsF of stable episulfonium ions obtained in one or two steps from alkenes⁶.

On the other hand it has been reported that dimethyl(methylthio)-sulfonium salts⁷ can be directly added to alkenes to form episulfonium salts⁸. Furthermore these episulfonium salts are opened *in situ* with various types of nucleophiles giving carbon-sulfur⁹, carbon-nitrogen¹⁰, carbon-oxygen^{11,12} or carbon-carbon bonds^{11,12}.

We wish to report a direct fluoro methanesulfonylation of alkenes using dimethyl(methylthio)sulfonium fluoroborate (DMTSF)¹³ and triethylamine tris-hydrofluoride ($\text{Et}_3\text{N}/3\text{HF}$)¹⁴ which we have recently shown to be a versatile source of fluoride anions in ring opening of epoxides¹⁵, aziridines¹⁶, aziridinium ions¹⁷, as well as for the nucleophilic displacement of triflate group by fluoride¹⁸ and for halofluorination reactions of unsaturated compounds¹⁹.

The reaction of various types of olefins (cf. Table) with DMTSF/ Et_3N , 3HF lead to β -fluoroalkyl-methylthioethers²⁰ in good yields.



In a typical procedure, a solution of 10 mmol of the unsaturated compound in 20 ml methylene chloride is treated at 0°C under stirring with 11 mmol (2.16 g) dimethyl(methylthio)sulfonium fluoroborate. After 20 min. a slight excess of triethylamine tris-hydrofluoride in 10 ml of methylene chloride is added dropwise at 0°C and stirring is continued for at least 1 day at room temperature. Usual workup (pouring into ice water, neutralization, extraction, drying, evaporation of the solvent) and subsequent purification of the product by distillation or column chromatography yields the desired β -fluoroalkyl-methylthioethers in good yields (cf. Table).

Table : Addition of (DMSTF/Et₃N, 3HF) to alkenes

| Alkenes | β -fluoroalkyl-methylthioethers | yield % | reaction time (h) | b.p./torr or m.p. |
|---------|---------------------------------------|--|-------------------|--|
| | | 90 ^{a)} 70 ^{a)} 80 ^{b)} | 24 48 48 | 78-79°/15 56°/0.1 (80°/2) ⁴ liquid |
| | | 90 ^{b)} | 48 | liquid |
| | | 76 ^{a)} | 48 | 54°/0.1 |
| | | 90 ^{a)} d) 17 ^{c)} d) | 72 120 | 100°/0.1 d) |
| | | 96 ^{c)} d) | 17 | liquid |
| | | 95 ^{b)} d) | 4 | liquid |
| | | 95 ^{b)} | 5 | liquid |
| | | 90 ^{c)} d) | 2 | liquid |
| | | 96 ^{c)} d) | 24 | d) |

a) purified by red. pressure distillation ; b) isolated by column chromatography (kieselgel, petroleum ether) ; c) crude product ; d) moisture sensitive.

References and Notes

- 1 G.H. Schmid, in "Topics in Sulfur Chemistry" (A. Senning, Ed.), Georg Thieme Verlag, Stuttgart, 1977, vol. 3, p 100.
G.H. Schmid, D.G. Garratt, in "Chemistry of Double Bonded Functional Groups", Supplement A, Part 2 (S. Patai, Ed.), Wiley, Chichester, 1977, Chap. 9, especially p. 828.
W.A. Smit, N.S. ZEFIROV, I.V. Bodrikov, M.Z. Krimer ; Acc. Chem. Res., 12, 282 (1979).
- 2 E. Kühle, in "The Chemistry of the Sulfenic Acids", Georg Thieme Verlag, Stuttgart, 1973, p. 2.
- 3 C.L. Liotta, H.P. Harris ; J. Amer. Chem. Soc., 96, 2250 (1974).
P. Tannhauser, R.J. Pratt, E.V. Jensen ; J. Amer. Chem. Soc., 78, 2658 (1956).
- 4 J.C. Carretero, J.L. Garcia-Ruano, M.C. Martinez, J. Rodriguez ; J. Chem. Res. (S) 6 (1985), (M) 0172-0194 (1985).
- 5 A.S. Gybin, W.A. Smit, M.Z. Krimer, N.S. Zefirov, L.A. Novgorodtseva, N.K. Sadovaya ; Tetrahedron, 36, 1361 (1980).
- 6 D.J. Pettitt, G.K. Helmkamp ; J. Org. Chem., 29, 2702 (1964).
- 7 For the structure and spectroscopic behavior of such salts cf. R. Minkwitz, H. Prenzel, H. Pritzkow ; Z. Naturforsch., 42b, 750 (1987).
- 8 G. Capozzi, O. De Lucchi, V. Lucchini, G. Modena ; Tetrahedron Letters, 2603 (1975).
- 9 G.K. Helmkamp, B.A. Olsen, D.J. Pettitt ; J. Org. Chem., 30, 676 (1965).
G.K. Helmkamp, B.A. Olsen, J.R. Koskinen ; J. Org. Chem., 30, 1623 (1965).
M.C. Caserio, C.L. Fischer, J.K. Kim ; J. Org. Chem., 50, 4390 (1985).
- 10 B.M. Trost, T. Shibata ; J. Amer. Chem. Soc., 104, 3225 (1982).
M.C. Caserio, J.K. Kim ; J. Amer. Chem. Soc., 104, 3231 (1982).
- 11 B.M. Trost, T. Shibata, S.J. Martin ; J. Amer. Chem. Soc., 104, 3228 (1982).
- 12 B.M. Trost, S.J. Martin ; J. Amer. Chem. Soc., 106, 4263 (1984).
- 13 H. Meerwein, K.F. Zenner, R. Gipp ; Liebigs Ann. Chem., 688, 67 (1965).
S.H. Smallcombe, M.C. Caserio ; J. Amer. Chem. Soc., 93, 5826 (1971).
- 14 R. Franz ; J. Fluorine Chem., 15, 423 (1980).
- 15 G. Alvernhe, A. Laurent, G. Haufe ; J. Fluorine Chem., 34, 147 (1986).
- 16 G.M. Alvernhe, C.M. Ennakoua, S.M. Lacombe, A.J. Laurent ; J. Org. Chem., 46, 4938 (1981).
- 17 D. Picq, D. Anker, C. Rousset, A. Laurent ; Tetrahedron Letters, 24, 5619 (1983).
- 18 D. Picq, D. Anker ; Carbohydr. Res., 166, 309 (1987).
- 19 G. Haufe, G. Alvernhe, A. Laurent ; Tetrahedron Letters, 27, 4449 (1986).
G. Alvernhe, A. Laurent, G. Haufe ; Synthesis, 562 (1987).
G. Alvernhe, D. Anker, A. Laurent, G. Haufe, C. Beguin ; submitted for publication to Tetrahedron.
- 20 The structures of the compounds were mainly determined by ^1H -, ^{13}C - and ^{19}F - high field NMR spectroscopic studies and by elemental analyses in the case of stable compounds.