Letters to the Editor

Exchange of a fluorosulfato group for fluorine in secondary β-fluorosulfonyloxyperfluoroalkyl radicals

*E. A. Avetisyan, B. L. Tumanskii, V. F. Cherstkov, and S. R. Sterlin**

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085. E-mail: srs@ineos.ac.ru

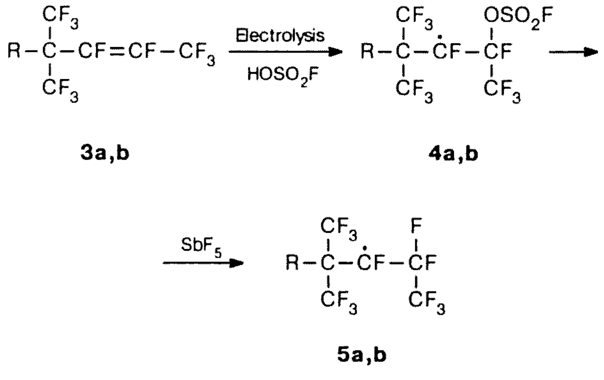
We have shown previously[1] that the action of SbF_5 results in the transformation of a (fluorosulfonyloxytetrafluoroethyl)(perfluorodiisopropyl)methyl radical (**1**)[2] into a perfluoroethyldiisopropylmethyl radical (**2**),[3,4] the product of substitution of the FSO_3 group in **1** by the fluorine atom. The anionoid mobility of the FSO_3 group in the initial radical was assigned to the stabilization of the conjugated carbocation by the vicinal paramagnetic center.

In the present work, it is established that secondary β-fluorosulfonyloxyperfluoroalkyl radicals (**4a,b**) generated during the electrochemical fluorosulfation of olefins (**3a,b**), also enter the exchange reaction with SbF_5, like tertiary radical **1**, to give the corresponding fluoroalkyl radicals **5a,b** (Scheme 1).

Radicals **4a,b** were obtained by electrolysis of a mixture of the corresponding olefin (40 g) and HSO_3F (50 mL) containing FSO_3Na (2 g) in an undivided cell (glass-carbon SU2000 as the anode, titanium as the cathode). After 0.01 F of electricity was passed (I = 0.6 A, t = 0.5 h), the organic layer containing, according to the ESR data, ~2—3 % of fluorosulfonyloxyperfluoroalkyl radical **4** (the concentration was determined by comparing the intensity of the signal in the solution under study with that in the solution of radical **1** with the known concentration in perfluorodibutyl ether) was separated and placed into an ESR tube. Excess SbF_5 was added, and the mixture was stirred. Only the signals of radicals **5** were registered in the ESR spectrum of the mixture obtained. Radicals **4** and **5** are unstable in the presence of oxygen, and they were not isolated preparatively.

The following hyperfine constants (HFC) of an unpaired electron with nuclei of fluorine atoms correspond to the ESR spectrum of radical **4a** described previously[5] (Fig. 1, *a*): $a_{\alpha\text{-F}}$(1 F) = 64.5, $a_{\beta\text{-F}}$ (2 F) = 15.1 G. The

Scheme 1



R = F (**a**); CF_3 (**b**)

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 4, pp. 1029—1030, April, 1996.

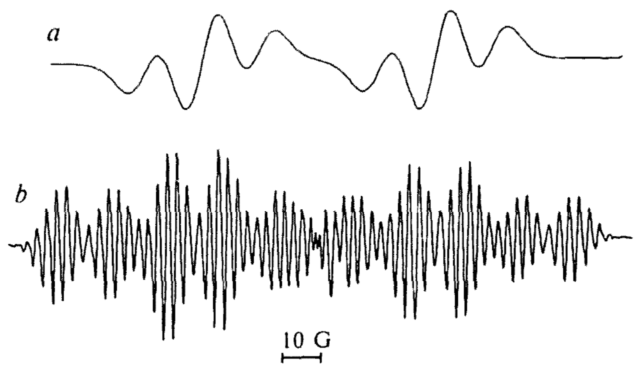


Fig. 1. ESR spectra of radicals **4a** (*a*) and **4b** (*b*).

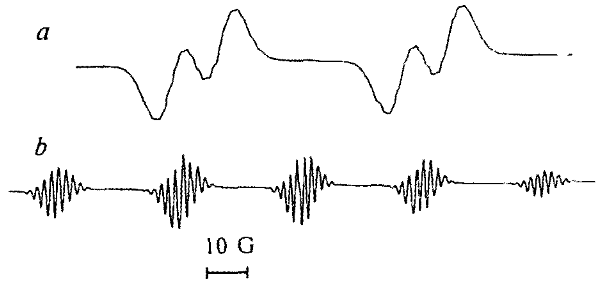


Fig. 2. ESR spectra of radicals **5a** (*a*) and **5b** (*b*). The decrease in the intensity of multiplets in the high-field spectral region is associated with the slow decay of the radical (time of recording is 4 min).

parameters of radical **5a** (Fig. 1, *b*) coincide with those of the radical obtained[6] by the fluorination of olefin **3a**: $a_{\alpha\text{-F}}$(1 F) = 67.0, $a_{\beta\text{-F}}$ (1 F) = 14.0, $a_{\beta\text{-F}}$(2 F) = 29.9, $a_{\gamma\text{-F}}$(9 F) = 2.6 G. Radicals **4b** and **5b** (Fig. 2, *a*) are characterized by the following parameters: **4b**. $a_{\alpha\text{-F}}$(1 F) = 61.5, $a_{\beta\text{-F}}$(1 F) = 10.5 G. **5b**. $a_{\alpha\text{-F}}$(1 F) = 64.5, $a_{\beta\text{-F}}$(2 F) = 33.2 G.

Thus, the new data obtained show that the substitution of the FSO_3 group by fluorine in β-fluorosulfonyloxyperfluoroalkyl radicals under the action of SbF_5 has a general character. It is based on the stabilization of the positive charge on the carbon atom, at which the substitution occurs, by the paramagnetic center, which provides the anionoid mobility of the fluorosulfate group.

This work was financially supported by the International Science Foundation (Grant MO 2300) and the Russian Foundation for Basic Research (Project No. 95-0308795).

References

1. E. A. Avetisyan, B. L. Tumanskii, V. F. Cherstkov, S. R. Sterlin, and L. S. German, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 576 [*Russ. Chem. Bull.*, 1995, **44**, 558 (Engl. Transl.)].
2. V. F. Cherstkov, E. A. Avetisyan, B. L. Tumanskii, S. R. Sterlin, N. N. Bubnov, and L. S. German, *Izv. Akad. Nauk, Ser. Khim.*, 1990, 2450 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1990, **39**, 2223 (Engl. Transl.)].
3. K. V. Scherer, Jr., T. Ono, K. Yamonouchi, R. Fernandez, P. Henderson, and H. Goldwhite, *J. Am. Chem. Soc.*, 1985, **107**, 718.
4. T. Ono, M. Terasawa, H. Fukaya, Y. Hayakawa, and T. Abe, *14-th Intern. Symp. on Fluorine Chem.*, Yokohama, 1994, 4C05.
5. V. M. Rogovik, A. F. Aerov, N. I. Delyagina, V. F. Cherstkov, S. R. Sterlin, and L. S. German, *Izv. Akad. Nauk, Ser. Khim.*, 1992, 1005 [*Bull. Russ. Acad. Sci., Div. Chem. Sci.*, 1992, **41**, 794 (Engl. Transl.)].
6. P. J. Krusic and K. V. Scherer, Jr., *J. Fluor. Chem.*, 1987, **35**, 44.

Received December 6, 1995;
in revised form January 25, 1996

A new cage metalloorganosiloxane

M. M. Levitsky,* N. V. Karpilovskaya, A. N. Gavrilova, B. G. Zavin, and E. S. Shubina

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085

Cage metalloorganosiloxanes (MOS) synthesized to the present time contain Ni,[1] Co,[2,3] Zr,[4] Sn,[5] and other metals and both metallosiloxane (M—O—Si) and pure siloxane (Si—O—Si) fragments. We have synthesized a cage MOS containing only M—O—Si fragments by the consecutive addition of alternating Si—O and M—O

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 4, pp. 1031—1032, April, 1996.