added gradually. The reaction mixture was stirred for 1 h at 20 °C (5 % trimer **4** and 95 % perfluorodi-*tert*-butylacetylene **2**, GLC), poured onto ice, and the organic layer was distilled over concentrated H_2SO_4. Compound **2** (7 g, 66 %) was obtained, b.p. 95—98 °C, m.p. 27 °C. Found (%): C, 25.77; F, 74.58. $C_{10}F_{18}$. Calculated (%): C, 25.97; F, 74.02. ^{19}F NMR: −9.2 s (CF_3). MS, *m/z* (I_{rel}(%)): 462 $[M]^+$ (0.5); 443 $[M-F]^+$ (3); 374 $[M-CF_4]^+$ (9); 355 $[M-CF_4-F]^+$ (12); 305 $[M-F-2CF_3]^+$ (8); 286 $[M-2CF_4]^+$ (4); 255 $[C_7F_9]^+$ (3); 205 $[C_6F_7]^+$ (3); 167 $[C_6F_5]^+$ (3); 117 $[C_5F_3]^+$ (3); 93 $[C_3F_3]^+$ (1); 69 $[CF_3]^+$ (100).

A mixture of freshly calcinated CsF (0.02 g), anhydrous diglyme (5 mL), and perfluoro-*tert*-butylacetylene **1** (2 g) was stirred at 20 °C for 20 min, then the bottom layer was separated; distillation of the latter gave **4** (1.5 g, 75 %), b.p. 77 °C (10 Torr). Found (%): C, 27.57; F, 72.25. $C_{18}F_{30}$. Calculated (%): C, 27.48; F, 72.52. ^{19}F NMR: −19.3 dec. ($3F^a$), −12.7 q ($9F^b$), −11.7 s ($9F^c$), −9.3 s ($9F^d$); J_{a-b} = 7 Hz. MS, *m/z* (I_{rel}(%)): 786 $[M]^+$ (10); 767 $[M-F]^+$ (15); 717 $[M-CF_3]^+$ (2); 672 $[C_{17}F_{25}]^+$ (5); 629 $[C_{16}F_{23}]^+$ (15); 567 $[C_{14}F_{21}]^+$ (4); 541 $[C_{15}F_{19}]^+$ (3); 479 $[C_{13}F_{17}]^+$ (3); 429 $[C_{12}F_{15}]^+$ (2); 341 $[C_{11}F_{11}]^+$ (2); 181 $[C_4F_7]^+$ (2); 69 $[CF_3]^+$ (100).

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The fluorosulfatoperfluoroalkyl radical: a new type of perfluoroalkylating reagent

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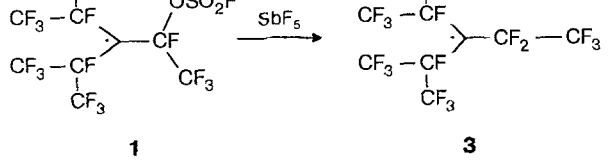
Previously, we have shown that the reaction of radical **1** with CsF in the absence of a solvent affords the perfluoroacetyl(diisopropyl)methyl radical (**2**), which is the product of the cleavage of the CF—OSO_2F group.[1]

The cleavage of the CF—OSO_2F group in radical **1** and its conversion to the keto group under the action of F^- is in accordance with the data on the reactivity of secondary perfluoroalkylfluorosulfates with respect to nucleophilic reagents.[2] Perfluorinated ketones are formed from secondary perfluoroalkylfluorosulfates under the action of SbF_5.[3] However, the reaction of radical **1** with SbF_5 gave not the expected keto radical **2**, but perfluoroisononyl radical **3**, which is the product of the replacement of the FSO_3 group by the fluorine atom, in more than 70 % yield.



1 **3**

In the series of fluoroaliphatic fluorosulfates, the FSO_3 group exhibits the properties of a leaving group only in the presence of fragments that can enhance the stability of the conjugated carbenium ion, *e.g.*, a vinyl or substituted vinyl group, capable of forming double-electron, three-center π-system, *i.e.*, allyl cation, with the carbon atom at which the substitution takes place.

The replacement of the fluorosulfato group in radical **1** is possible only if radical cation **4** also possesses enhanced stability. It is evident in this case that the radical center is the stabilizing factor, because it forms a one-electron double-centered π-system with the carbon atom at which the substitution takes place (vinyl radical cation **4** was observed in the mass spectrum of perfluoromethyl(diisopropyl)ethylene).

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Hence, it was shown that the paramagnetic center, like the other structural fragments possessing enhanced

† Deceased.

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electron density, is capable of interacting with the neighboring carbon atom, thus increasing the stability of the carbenium ion and making it possible to replace a potential leaving group.

This alkylating ability of fluorosulfatoperfluoroisononyl radical **1** stimulated us to reinvestigate its reaction with CsF. It is known that, depending on the reaction conditions,fluoroaliphatic fluorosulfates, in which the fluorosulfate group is activated by the adjacent sp^2-hybridized carbon atom, are able to exhibit ambident reactivity depending on the nucleophilic reagents, *i.e.*, fluorosulfonating activity in the absence of a solvent and alkylating activity in the presence of an aprotic, polar solvent. One would expect that radical **1** in the reaction with CsF in a solvating medium also would exhibit alkylating activity. In fact, the reaction of **1** with CsF in the presence of a small amount of acetonitrile affords radicals **2** and **3** in comparable yields (according to ESR spectroscopy).

A mixture of radical **1** (10 g, 18 mmol) and SbF_5 (4 g, 20 mmol) was heated for 45 min with a gradual increase in temperature from 30 to 60 °C. The reaction mixture was poured onto ice, the organic layer was dried over $MgSO_4$, and distilled, giving radical **3** (6.1 g, 75 %), b.p. 41—43 °C (40 Torr). Found (%): C, 22.92; F, 76.94. C_9F_{19}. Calculated (%): C, 23.03; F, 76.97. The ESR spectrum is identical with that described for the perfluoroethyl(diisopropyl)methyl radical.[4]

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