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Stable fluoroaliphatic radicals containing functional groups: synthesis and reactivity

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Abstract

β-Fluorosulphatoperfluoroalkyl radicals (**3**, **7** and **8**) are obtained by the reaction of fluoroolefins (HFP trimer and dimer, and perfluoro-4,4-dimethylpent-2-ene, respectively) with $(FSO_3)_2$. The pure β-fluorosulphatotetrafluoroethylperfluorodiisopropylmethyl radical (**3**) has been isolated and converted to the perfluoroacetyldiisopropylmethyl radical (**4**) under the action of CsF. The reaction of radicals **3**, **7** and **8** with SbF_5 leads to the replacement of the FSO_3 group by a fluorine atom. The ability of the FSO_3 group in β-fluorosulphatoperfluoroalkyl radicals to play the role of a leaving group is explained by the stabilizing effect of the unshared electron on the adjacent carbocation centre.

Keywords: Fluoroaliphatic radicals; Synthesis; Reactivity; ESR spectroscopy

1. Introduction

Although the formation of stable aliphatic C-centred radicals (SACCR) unstabilized by conjugation has been recorded repeatedly by ESR methods [1], the preparative synthesis of such radicals has only been performed in the case of the perfluoroethyldiisopropylmethyl radical (**2**) obtained during the fluorination of perfluoro-3-isopropyl-4-methylpentene-2 (**1**) [2,3]. The preparative synthesis of SACCR containing functional groups had not been described in the literature until our papers were published [4,5]. Here we report the synthesis and isolation of a functionalized SACCR, the β-fluorosulphatotetrafluoroethyldiisopropylmethyl radical (**3**), produced by the radical fluorosulphation of olefin **1**. The perfluoroacetyldiisopropylmethyl radical (**4**) was obtained by the interaction of **3** with CsF, and radical **2** by the reaction of **3** with SbF_5. Chemical transformations of radicals **3**, **7** and **8** (see below) with retention of the radical centre make it possible to establish the influence of the radical centre on the reactivity of a neighbouring functional group.

2. Results and discussion

The influence of molecular moieties containing a double bond (i.e. two π-electrons in the field of two sp^2-hybridized carbon atoms) on the reactivity of neighbouring functional groups is well known and predictable to a great extent. How does a radical centre (one p_z electron in the field of one sp^2-hybridized carbon atom) affect functional groups located in the β-position to the radical centre?

Is it obvious that radicals intended for such investigations must meet the following requirements.

(i) They must have a functional group in the vicinal position to the radical centre localized on the carbon atom.

(ii) They must be sufficiently stable to make it possible to perform their synthesis on a preparative scale and to use them as reagents in common chemical reactions.

(iii) They must not contain fragments capable of being involved in delocalization of the unpaired electron and, thus, distort its possible influence on the reactivity of the neighbouring functional group.

We considered the radical addition of peroxydisulphuryl difluoride (PSF) to higher branched fluoroolefins to be the most promising method for the synthesis of such radicals as could meet the specified requirements. We would expect their stability to be attributed to the high steric hindrance of the radical centre which allowed the successful synthesis of the perfluoroisononyl radical **2**; the FSO_3–C–F group formed in the addition of the FSO_3 radical to the double bond can be easily converted to a carbonyl group by the action both of nucleophilic [6] and electrophilic agents [7].

In fact, the interaction of the hexafluoropropene trimer **1** with PSF afforded the stable α-fluorosulphatotetrafluoroethyl

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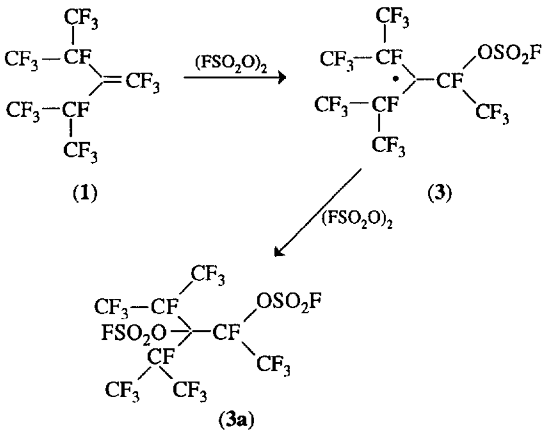
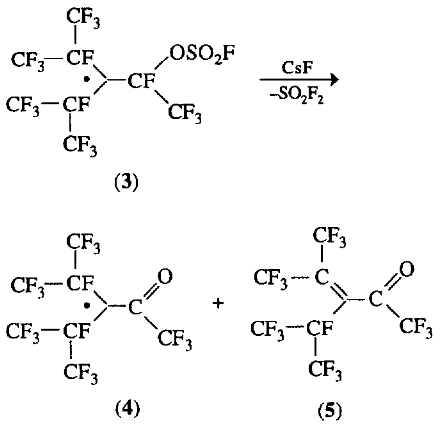
perfluorodiisopropylmethyl radical (**3**) (at a 1:0.5 molar ratio of **1** and PSF). Radical **3** was also obtained by the electrolysis of HSO_3F in the presence of **1** (ca. 0.3 F per mole of **1**). An increase in the quantity of PSF or the electrolysis time resulted in the formation of the vicinal bis-fluorosulphate **3a**. The significant difference in boiling points of the starting olefin **1**, radical **3** and the product **3a** allows **3** to be readily isolated from the reaction mixture (Fig. 1).



Interaction of **3** with CsF leads to the keto radical **4**, the product of cleavage of the O–S and C–F bonds, which is obtained as a 70% material (according to iodometry data) containing vinylketone **5** as the main byproduct. To our knowledge this reaction is the first example to the chemical conversion of an aliphatic C-centred radical with retention of the radical centre, leading to formation of one more aliphatic stable C-centred radical containing a functional group (Fig. 2).



Conversion of the FSO_3CF group in radical **3** to the carbonyl by the action of fluoride ion is consistent with commonly accepted ideas concerning the reactivity of secondary perfluorinated fluorosulphates with respect to nucleophilic agents [6]. Perfluorinated ketones can be also formed from secondary perfluorinated fluorosulphates by the action of SbF_5 [7]. However, the reaction of **3** with SbF_5 led unexpectedly to the formation of the perfluoroisononyl radical **2**, the product of substitution of the FSO_3 group by fluorine, instead of the expected keto radical **4**, the product of FSO_3CF group cleavage (Fig. 3) [13].

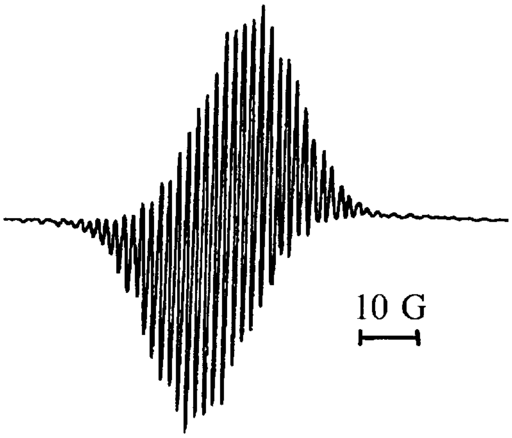
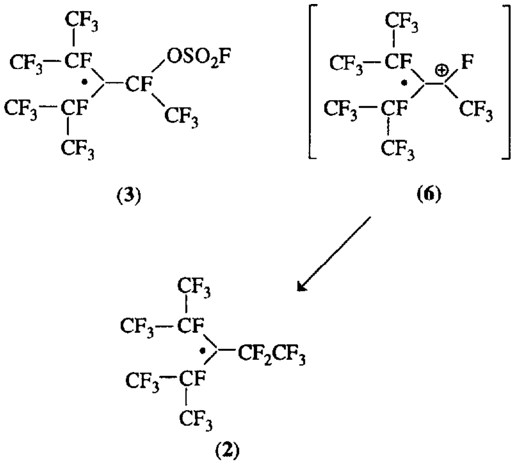


Fig. 1. ESR spectrum of radical **3** at 50 °C (solvent: perfluorodibutyl ether). Isotropic hyperfine splitting (G) in **3**: $a_{F\text{-}\beta}(3F)=3.75$, $a_{F\text{-}\gamma}(12F)=2.75$, $a_{F\text{-}\gamma}(3F)=1.25$.



An FSO_3 group in fluoroaliphatic fluorosulphates may only be a leaving group in those cases when a molecule contains moieties capable of increasing the stability of the corresponding carbonium ions, for example, vinyl or substituted vinyl groups forming a relatively stable three-centred π-system, allylic carbocation, with the carbon atom at which the substitution occurs [8,9].

Substitution of the FSO_3 group in radical **3** is possible provided that the cation-radical **6** is also sufficiently stable. It is obvious that in this case the paramagnetic centre is a stabilizing factor which forms a relatively stable one-electron two-centred π-system with the carbon atom bearing the positive charge. Such a particle vinyl cation-radical **6** is recorded in the mass spectrum of olefin **1**. Thus, the similarity in chemical behaviour of radical **3** and perfluorinated α,β-unsaturated fluorosulphates indicates a definite similarity in the effect of a free valency and a double bond on the reactivity of the adjacent group. The general character of this reaction is confirmed by the formation of the perfluoroalkyl radicals **9** and **10** from the β-fluorosulphatoperfluoroalkyl radicals **7**

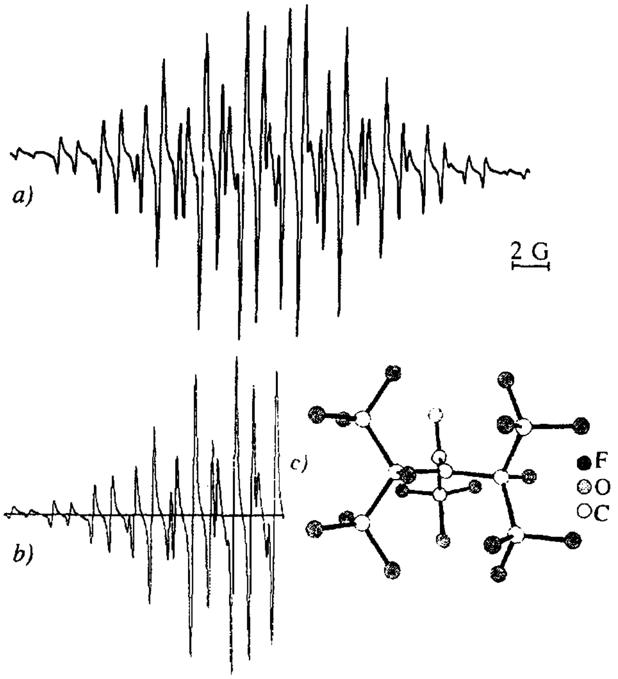
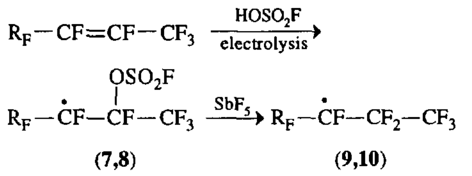


Fig. 2. (a) ESR spectrum of radical **4** at 50 °C (solvent: perfluorodibutyl ether). Isotropic hyperfine splitting (G) in **4**: $a_{F\text{-}\nu}(2F)=a_{F\text{-}\gamma}(12F)=2.3$, $a_{F\text{-}\gamma}(3F)=3.3$. (b) Computational simulation of the spectrum of **4**. (c) Conformation of radical **4** corresponding to energy minimum as calculated by the MMX2 program.

and **8** under the action of SbF_5. The ESR spectra of these various radicals and associated data are depicted in Figs. 4 and 5.



$$R_F-CF{=}CF-CF_3 \xrightarrow[\text{electrolysis}]{HOSO_2F}$$

$$\underset{(\mathbf{7,8})}{R_F-\dot{C}F-\overset{\overset{OSO_2F}{|}}{C}F-CF_3} \xrightarrow{SbF_5} \underset{(\mathbf{9,10})}{R_F-\dot{C}F-CF_2-CF_3}$$

7, **9**: $R_F = i\text{-}C_3F_7$; **8**, **10**: $R_F = t\text{-}C_4F_9$

The alkylating ability of radical **3** (which we have found) has made us reconsider its reaction with CsF. It is well known that fluoroaliphatic fluorosulphates containing the FSO_3 group activated by a neighbouring sp^2-hybridized carbon atom are able to show ambident reactivity with respect to nucleophilic reagents depending on the reaction conditions: they reacts as fluorosulphonating agents in the absence of solvents and as alkylating agents in polar aprotic media [9]. We suggest that radical **3** will behave as an alkylating agent in a solvating medium. In fact, the addition of several drops of MeCN to a mixture of **3** and CsF leads to the appearance of the signals of both radicals **4** and **2** in the ESR spectrum. When the reaction is carried out in dilute acetonitrile solution, only the signal of radical **2** is recorded in the ESR spectrum. Under these conditions the ketoradical **4** is unstable as was shown by a special experiment.

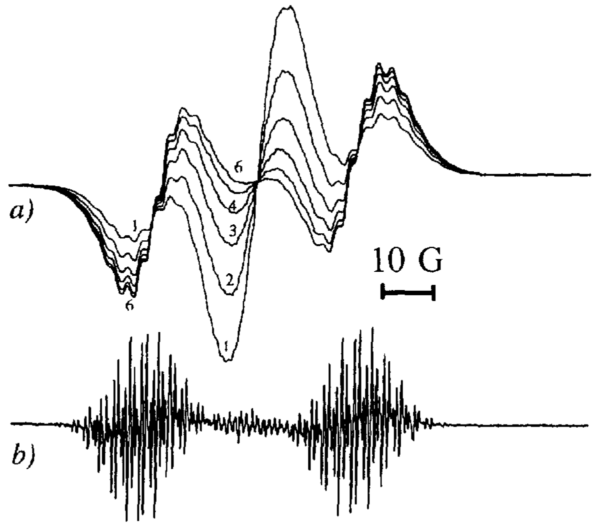


Fig. 3. (a) The kinetics of the conversion of radical **3** to radical **2** by the action of SbF_5 at 80 °C (solvent: perfluorodibutyl ether). Recorded within an interval of 4 min. (b) ESR spectrum of radical **2** recorded after a 100-fold dilution of the reaction mixture.

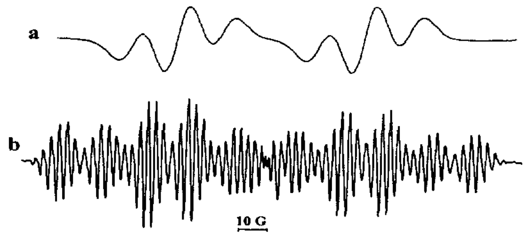


Fig. 4. (a) ESR spectrum of radical **7** [11] at 25 °C (solvent: perfluoro-4-methylpent-2-ene). Isotropic hyperfine splitting (G): $g_{F\text{-}\alpha}(1F)=64.5$, $a_{F\text{-}\beta}(2F)=15.1$. (b) ESR spectrum of radical **9** at 25 °C (solvent: perfluoro-4-methylpent-2-ene) (first prepared by fluorination of HFP dimer [12]). Isotropic hyperfine splitting (G): $g_{F\text{-}\alpha}(1F)=67.0$, $a_{F\text{-}\beta}(1F)=14.0$, $a_{F\text{-}\beta}(2F)=29.9$, $a_{F\text{-}\chi}(9F)=2.6$.

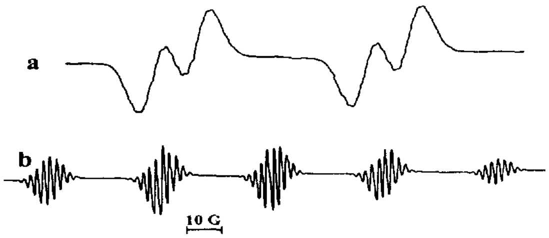


Fig. 5. (a) ESR spectrum of radical **8** at 25 °C (solvent: perfluoro-4,4-dimethylpent-2-ene). Isotropic hyperfine splitting (G): $a_{F\text{-}\alpha}(1F)=61.5$, $a_{F\text{-}\beta}(1F)=10.5$. (b) ESR spectrum of radical **10** at 25 °C (solvent: perfluoro-4,4-dimethylpent-2-ene). Isotropic hyperfine splitting (G): $a_{F\text{-}\alpha}(1F)=64.5$, $a_{F\text{-}\beta}(2F)=32.2$. A decrease in intensity of the multiplets in the highfield region of the spectrum is attributed to the slow decay of the radical (sweep time, 4 min).

3. Experimental details

3.1. Preparation of the β-fluorosulphatotetrafluoroethyldiisopropylmethyl radical 3

Peroxydisulphuryl difluoride (PSF) (3.2 g, 16 mmol) was added to hexafluoropropene trimer (7.7 g, 22 mmol) at 0–5

°C and the reaction mixture stored at room temperature for 5 d. Distillation gave 7.2 g (78% yield) of **3**, b.p. 54–56 °C/12 mmHg. IR (ν, cm^{-1}): 1490 (SO_2F).

3.2. Preparation of the perfluoroacetyldiisopropylmethyl radical 4

A mixture of **3** (6 g, 11 mmol) and CsF (1 g, 6 mmol) was stirred at 45–60 °C for 4 h. The volatile products were evacuated in vacuo into a trap (−78 °C) and distilled at 35–37 °C/50 mmHg to give 3.7 g (75% yield) of a fraction (as a brown–black liquid) which contained ca. 70% **4** (according to iodometric data) with vinylketone **5** as the main byproduct. IR (ν, cm^{-1}): for **4**: 1775, 1740 (C=O); for **5**: 1780 (C=C); 1630 (w) (C=C) {lit. IR data for **5**: 1770 (s) (C=O); 1630 (w) (C=C) [10]}.

3.3. Preparation of the perfluoroethyldiisopropylmethyl radical 2

A mixture of **3** (10 g, 18 mmol) and SbF_5 (4 g, 20 mmol) was stirred at 30–60 °C for 45 min and poured into crushed ice. The organic layer was separated, dried over $MgSO_4$ and distilled to give **2** (6.1 g, 75% yield), b.p. 41–43 °C/40 mmHg (lit. data 37–37.5 °C/35 mmHg [3]).

3.4. Preparation of the β-fluorosulphatoperfluoroalkyl radicals 7 and 8

These radicals were obtained by the electrolysis of a mixture of the corresponding olefin (hexafluoropropene dimer and perfluoro-4,4-dimethyl-2-pentene [14]) (40 g) and HSO_3F (50 ml) containing 2 g of FSO_3Na. After electrolysis ($I = 0.6$ A; time = 0.5 h) the organic layer contained ca. 2%–3% of the fluorosulphatoperfluoroalkyl radicals according to ESR spectroscopic data (the concentration was determined by a comparison of the intensity of the signal for the solution examined with that for the solution of radical **3** at a given concentration in perfluorodibutyl ether).

3.5. Preparation of the perfluoroalkyl radicals 9 and 10

The organic layer from the electrolysis described in Section 3.4 was separated and treated with an excess of SbF_5 at room temperature. The ESR spectrum of the resulting solution only exhibited signals corresponding to the perfluoroalkyl radicals **9** and **10**. Since these radicals are unstable in the presence of oxygen, their isolation on a preparative scale was not attempted.

Acknowledgements

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