Synthesis of a persistent perfluoroalkyl radical by electrochemical fluorination

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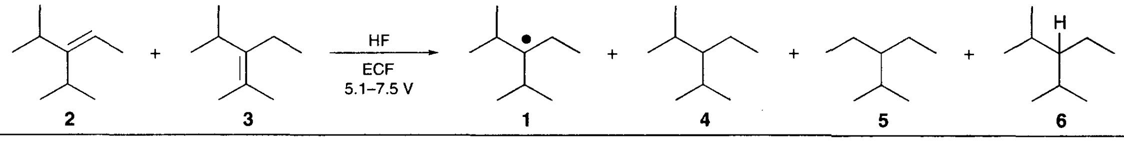
A persistent perfluoroalkyl radical, perfluoro-3-ethyl-2,4-dimethyl-3-pentyl, was synthesized by the electrochemical fluorination of a mixture of hexafluoropropene trimers in the presence of a large amount of sodium fluoride.

It is known that the persistent perfluoroalkyl radical (PFR) **1**, perfluoro-3-ethyl-2,4-dimethyl-3-pentyl, which is stable enough to be analysed by GC, can be synthesized by direct fluorination of hexafluoropropene trimers, perfluoro-3-isopropyl-4-methylpent-2-ene **2** and perfluoro-3-ethyl-2,4-dimethylpent-2-ene **3**, in high yield[1]. It has recently been reported[2] that different kinds of PFRs can be prepared by a conventional electrochemical fluorination (ECF) method instead of using fluorine gas. We are interested in the ECF of **2** and **3** from both synthetic and mechanistic points of view. A literature survey shows that there is a prior patent work[3] on the ECF of **2** and **3**, which claimed that two perfluorinated products, perfluoro-3-ethyl-2,4-dimethylpentane **4** and perfluoro-3-ethyl-2-methylpentane **5**, were obtained in 29 and 62.3% yields, respectively, but gave no description on the formation of PFR **1**. We traced the experiment carefully and found new products **6** and PFR **1** in addition to the above two products. Here we show the synthesis of PFR **1** by highlighting the important role of sodium fluoride in the successful formation of PFR **1** in the ECF process.

ECF was conducted on a 2:3 mixture of **2** and **3** using a typical Simons process[4] in a 500 ml cell equipped with nickel electrodes. All products obtained were isolated by GC and the structures were elucidated by ^{19}F NMR and mass spectra except **1** (EPR instead of NMR). Yields were calculated from the peak areas as a percentage of the total peak area.† The results are summarized in Table 1. At first ECF was conducted in the absence of sodium fluoride, which the patent claims is critically important for better yield. The main products, **4** and **5**, were obtained in a *ca.* 1:2 ratio as reported in the patent, and additionally, PFR **1** was found to be obtained in 2% yield along with another new product **6** in 8.7% yield (run 1). We repeated the same experiment with added sodium fluoride in order to increase conductivity. When 5 g of sodium fluoride was used the yield of PFR **1** increased to 7.3% with reduction of the yields on **4** and **5** (run 2). Interestingly, the yield of **6** also increased from 8.7 to 13.7%. Recovery of the starting material increased remarkably (12.6% for run 1 and 41.9% for run 2). Next we conducted the same ECF until almost all the starting material was consumed (run 3). The yield of **1** increased again (11.8%), and a striking increase was observed in the yield of **6**, from 13.7 to 33.7%, which seems to be reasonable considering its formation mechanism (*vide post*). A drastic increase in the amount of sodium fluoride used (×10), has a big effect on the product distribution, thus resulting in the partial suppression of formation of **4**, **5**, and **6** (run 5). However, the yield of **1** remained largely unchanged (11.6%). It should be pointed out that a large amount of the starting material was recovered (67.2%), which means the yield of **1** based on the consumed material is rather high (35.4%). A further drastic increase in the amount of sodium fluoride used (×22), led to the selective formation of **1** with total suppression of the formation of **4**, **5**, and **6** (run 6). However, the yield of **1** was reduced despite the high selectivity.

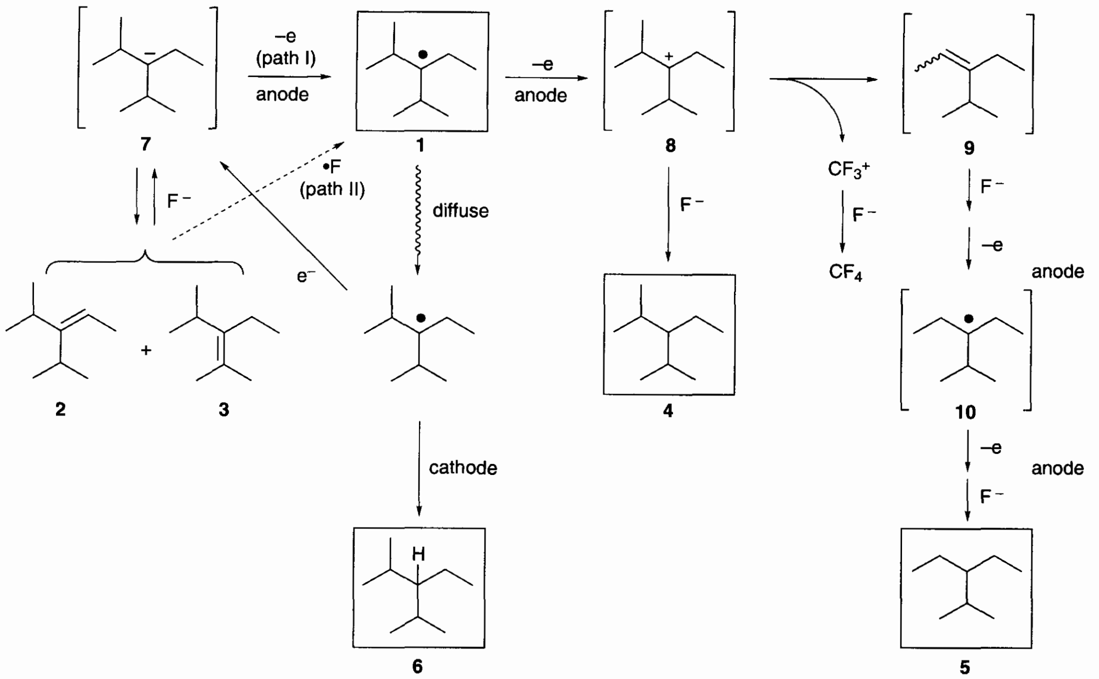
The mechanism for the formation of **1** is proposed in Scheme 1. At first, we postulated that the existence of fluoride ion catalysed the equilibrium between the anion **7** and the starting **2** and **3**, which may be shifted toward anion formation by the addition of excess sodium fluoride, and that the formed anion **7** discharges an electron on the surface of the anode to give the PFR **1** (path I). This postulation is attractive because the role of sodium fluoride is clearly explained for the formation of **1**, but there seems to be a contradiction with regard to the formation of the product **6**. The probable mechanism for the formation of **6** is as follows. The radical **1** formed on the surface of the anode is resistant to further fluorination, detaches from the anode surface and moves onto the cathode surface, where reduction occurs to give the anion **7** which then combines with H^+ to give **6**. If this is true, the anion **7** formed directly from the starting **2** and **3** by the action of fluoride ion should take up H^+ to give **6**, vigorously competing with the radical formation pathway. However, vigorous stirring of a two phase mixture comprising a concentrated anhydrous hydrogen fluoride solution of sodium fluoride and the starting **2** and **3** at room temperature over several days gave no sign of the formation of

Table 1 Synthesis of persistent perfluoroalkyl radical **1** by ECF method (all unmarked bonds are to fluorines)



Run	NaF/g	Passed electricity/ Ah	Yield (%) **1**[a]	**4**	**5**	**6**	Recovery of **2** and **3** (%)
1	—	25.5	2.0 (2.3)[a]	16.9	40.5	8.7	12.6
2	5	26	7.3 (12.6)	9.4	20.3	13.7	41.9
3	5	51	11.8 (12.0)	15.1	26.4	33.7	2.0
4	5	10	2.8 (10.0)	0.6	2.0	2.2	73.0
5	50	26	11.6 (35.4)	2.6	5.0	1.7	67.2
6	110	26	5.5 (18.9)	—	—	—	70.9

[a] The yields based on **2** and **3** consumed are in parentheses. All yields are calculated from GC analyses.



Scheme 1 Reaction mechanism of the ECF process of a mixture of **2** and **3**; Intermediates are in brackets and the products are in boxes. All unmarked bonds are to fluorines.

6. This result suggests that there is no such equilibrium or that the protonation of the anion **7** is an unfavourable process under these conditions. If the former is right, a different mechanism must be devised for the formation of **1**, and we therefore describe a fluorine radical scheme (path II) for the process, but by adopting this radical scheme the role of sodium fluoride becomes obscure. If the latter is true, then another mechnism must be presented for the formation of **6**. The most probable is the hydrogenation at the cathode surface. This idea is consistent with the fact that the yield of **6** increased at the expense of **1** by the reductive process with the increase of passed electricity (runs 2–4) and does not contradict the role of the sodium fluoride mentioned above.

It is known that the radical **1** decomposes on a gentle heating ($T_{1/2}$ = 60 min at 100 °C),[1] eliminating trifluoromethyl radical and giving a mixture of *cis*- and *trans*-perfluoroalkenes **9**. Since the ECF was conducted at rather low temperature (near 0 °C), this thermal process is less likely, even though not rigorously excluded. The trifluoromethyl fragment from the decomposition of **1** to **9** was quantitatively recovered as tetrafluoromethane in a liquid nitrogen trap.‡ Both formation of **9** and tetrafluoromethane as well as the formation of **4** and **5** can be explained by the carbocation mechanism (ECEC).[5] Although **9** and **10** were not isolated, it is reasonable that **5** was formed through **9** and **10**. No detection of the hydride form of **10** corresponding to **6** in the reaction mixture supports the simultaneous fluorination of **9** in its nascent state.

Footnotes

† Relative sensitivities of the compounds **1**–**6** against the FID are almost the same and not considered in the calculation of yields.

‡ The material trapped at −193 °C was ascertained as tetrafluoromethane by IR. The amount obtained in each run is as follows; run 1 (3.1 g), run 2 (1.4 g), run 3 (2.0 g), run 4 (nil), run 5 (0.6 g), run 6 (nil).

References

1 K. V. Scherer, T. Ono, K. Yamanouchi, R. Fernandez and P. Henderson, *J. Am. Chem. Soc.*, 1985, **107**, 718.
2 U. Gross, S. Rudiger and A. Dimitrov, *J. Fluorine Chem.*, 1996, **76**, 139.
3 S. Benninger, *GP* 2,302,132, 1974, (*Chem. Abstr.*, **81**, P151510q).
4 A memorial issue for J. H. Simmons, *J. Fluorine Chem.*, **32**, 1986, and references cited therein.
5 J. Burdon, I. W. Parsons and J. C. Tatlow, *Tetrahedron*, 1972, **28**, 43.

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