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autoclave and cooled to −75 °C. Ammonia gas was bubbled through the cold solution until ca. 30 mL was condensed; the volume of the solution at this point was ca. 50 mL. The autoclave was sealed and heated at 60 °C for 18 h. The ammonia and methanol were evaporated, and the residue was dissolved in dichloromethane (150 mL). The brown solution was washed with water, dried (K_2CO_3), filtered, and evaporated to dryness. The off-white residue was dissolved in a mixture of ether (20 mL), containing dichloro methane (2 mL). Seed crystals were added, and the solution was stirred at room temperature for 2 h at which time most of the product had crystallized. The suspension was cooled to 5 °C and filtered. The white solid was washed with cold ether and air-dried to give crystalline product **17b** (2.6 g). This material was recrystallized from a mixture of dichloromethane (2.5 mL) and ether (20 mL) to give pure **17b** (2.3 g, 70%): mp 120–123 °C; $[\alpha]^{24}_{\mathrm{D}}$ −57° (*c* 0.9, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.36 and 1.48 (s, 3 H, CH_3), 4.28 (s, 2 H, H-6′a,b), 4.63 (s, 2 H, OCH_2Ph), 4.74 (d, J = 5.5 Hz, 1 H, H-5′), 5.39 (d, J = 5.50 Hz, 1 H, H-4′), 5.58 (s, 1 H, H-1′), 5.83 (s, 1 H, H-2′), 6.61 (s, 2 H, NH_2), 7.34 (m, 5 H, Ph), 7.68 (s, 1 H, H-2), 8.35 (s, 1 H, H-8). Anal. Calcd for $C_{21}H_{23}N_5O_3$: C, 64.11; H, 5.89; N, 17.60. Found: C, 63.88, H, 6.13; N, 17.45.

(−)-Neplanocin A (2). The crystalline precursor **17b** (2 g, 5.1 mmol) was dissolved in dry dichloromethane (200 mL), and the solution was cooled with stirring to −75 °C. Boron trichloride in hexane (36 mL, 1 M solution) was added in one portion. The mixture was stirred at −75 °C for 2.5 h, after which time no starting material was observable by TLC. Methanol (40 mL) was added, and the clear solution was evaporated to dryness. The gummy residue was redissolved in methanol (20 mL), and the solution was evaporated; this procedure was repeated twice. The residual foam was refluxed with ether until a crystalline precipitate was obtained. After cooling, the supernatant was decanted, and the crystalline product was refluxed with a mixture of ethanol (5 mL) and ether (25 mL). The hot suspension was diluted with ether (25 mL) and cooled, and the crystalline (−)-neplanocin A hydrochloride was collected (1.8 g, a slightly hygroscopic solid). This material was dissolved in warm methanol (30 mL), and the cloudy solution was filtered through Celite. The clear filtrate was adjusted to pH 12 with ammonium hydroxide (10% aqueous solution), and the resulting solution was evaporated to dryness. The residue was refluxed with ethanol (20 mL), and crude (−)-neplanocin A (0.9 g) was separated after cooling. This material was recrystallized twice from boiling 75% aqueous ethanol to give 0.65 g (50%) of pure (−)-neplanocin A: mp 212–213 °C (lit.[5] mp 220–222 °C); $[\alpha]^{24}_{\mathrm{D}}$ −153.8° (*c* 0.3, H_2O) [lit.[5] $[\alpha]^{23}_{\mathrm{D}}$ − 157° (*c* 0.5, H_2O)]; ^1H NMR (Me_2SO-d_6/D_2O) δ 4.10 (s, 2 H, H-6′a,b), 4.22 (t, J = 5.5 Hz, H-5′), 4.40 (d, J = 5.5 Hz, 1 H, H-4′), 5.30 (br s, 1 H, H-1′), 5.67 (d, $J < 1$ Hz, 1 H, H-2′), 8.05 and 8.10 (s, 2 H, aromatic); ^{13}C NMR (Me_2SO-d_6/D_2O) δ 59.87, 65.88, 73.55, 78.27, 120.10, 126.30, 141.95, 150.20, 150.35, 153.62, 156.70; FAB MS, m/z (relative intensity) 356 (MH^+ glycerol, 10), 264 (MH^+, 100), 136 (b + 2H, 92). Anal. Calcd for $C_{11}H_{13}N_5O_3 \cdot 0.5H_2O$: C, 48.53; H, 5.18; N, 25.72. Found: C, 48.55; H, 5.13; N, 25.95.

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Electrochemical Oxidation of Polyfluoroalkyl Iodides: Direct Anodic Transformation of $C_8F_{17}CH_2CH_2I$ to Amides, Esters, and Ethers[†]

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The cyclic voltammetry of polyfluoroalkyl iodides of the type $R_fCH_2CH_2I$ (R_f = n-C_6F_{13}, n-C_8F_{17}, n-$C_{10}F_{21}$) and R_fI (R_f = n-C_4F_9, n-C_6F_{13}, n-C_8F_{17}, n-$C_{10}F_{21}$) was investigated in nonaqueous media. All the iodides exhibited one distinctive oxidation peak, but only $C_8F_{17}CH_2CH_2I$ was suitable for surveying preparative-scale electrosynthetic reactions because the other iodides either had poor solubility or caused severe filming of the anode. The direct anodic transformations of the iodide to the corresponding amides ($C_8F_{17}CH_2CH_2NHCOR$; R = CH_3, $CH{=}CH_2$, $C(Me){=}CH_2$), esters ($C_8F_{17}CH_2CH_2OCOR$; R = CH_3, CF_3, $CH{=}CH_2$, $C(Me){=}CH_2$, C_6H_5), ethers (mainly $C_8F_{17}CH_2CH_2OCH_2CF_3$), and alcohol ($C_8F_{17}CH_2CH_2OH$) were observed and a general mechanistic scheme involving a hypervalent iodanyl radical intermediate is proposed.

Introduction

Perfluoroalkyl and 2-(perfluoroalkyl)ethyl iodies, R_fI and $R_fCH_2CH_2I$, are important starting materials in organofluorine chemistry. Unconventional methods, however, often are required to replace the iodide with other functional groups since these fluoroalkyl iodides are prone to give elimination rather than substitution products. For example, 2-(perfluoroalkyl)ethanols $R_fCH_2CH_2OH$ cannot be made by displacement of the iodide with hydroxide ion since this produces almost exclusively the elimination products, $R_fCH{=}CH_2$. Instead, the alcohols are prepared by treatment of the corresponding iodide with oleum,[1-3] concentrated nitric acid,[4] heavy metal ions,[5] or amides.[6,7]

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(1) Day, R. I. U.S. Patent 3 283 012 (to E.I. du Pont de Nemours and Co.), November 1, 1966; *Chem. Abstr.* **1967**, *66*, 18507t.

(2) Mares, F.; Oxenrider, B. C. *J. Fluorine Chem.* **1976**, *8*, 373.

(3) Millauer, H. Ger. Offen. 2 318 677 (to Farbwerke Hoechst A.-G.), November 7, 1974; *Chem. Abstr.* **1975**, *82*, 72523p.

(4) Rebsdat, S.; Schuierer, E.; Ulm, K.; Wimmer, I. Ger. Offen. 2 028 459 (to Farbwerke Hoechst A.-G.), December 23, 1971; *Chem. Abstr.* **1972**, *76*, 58963b.

(5) (a) Seil, C. A.; Boschan, R. H.; Holder, J. P. U.S. Patent 3 246 030 (to Douglas Aircraft Co., Inc.), April 12, 1966; *Chem. Abstr.* **1966**, *64*, 19414g. (b) Blancou, H.; Benefice, S.; Commeyras, A. *J. Fluorine Chem.* **1983**, *23*, 57.

(6) Kornblum, N.; Smiley, R. A.; Blackwood, R. K.; Iffland, D. D. *J. Am. Chem. Soc.* **1955**, *77*, 6269.

0022-3263/88/1953-5714$01.50/0

Table I. Anodic Peak Potentials (V) at Different Scan Rates (mV/s)[a]

	mV/s				solvent–electrolyte (0.1 M)
compd	500	200	100	50	
$C_6F_{13}CH_2CH_2I$	1.61	1.56	1.55	1.50	$CH_3CN–Et_4NBF_4$ (TEAF)
$C_8F_{17}CH_2CH_2I$	1.49	1.42	1.39	1.39	CH_3CN–TEAF
$C_{10}F_{21}CH_2CH_2I$	*b*	*b*	2.15	2.10	CH_2Cl_2–*n*-Bu_4NBF_4 (TBAF)
C_4F_9I	1.63	1.58	1.53	1.48	CH_3CN–TEAF
$C_6F_{13}I$	1.62	1.59	1.56	*c*	CH_3CN–TEAF
$C_8F_{17}I$	2.03	1.91	1.56	*c*	CH_2Cl_2–TBAF
$C_{10}F_{21}I$	*b*	*b*	>1.70	1.65[d]	THF–TBAF

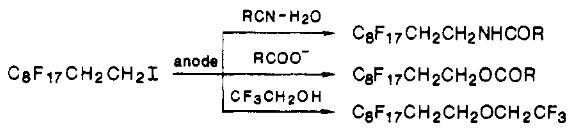
[a] All potentials are quoted vs Ag wire (+0.15 V vs SCE); working electrode, Pt button; counter electrode, Pt net cylinder. Potentials were scanned from 0 V positively to the onset of each solvent–electrolyte system. [b] All ill-defined wave. [c] Not recorded at this sweep rate. [d] E_p = 1.52 V at 20 mV/s.

Esters of $R_fCH_2CH_2OH$ can be prepared from $R_fCH_2CH_2I$ and carboxylic acid salts (for example, $Cd(OAc)_2$[8] or triethylammonium fumarate[9]) by phase-transfer-catalyzed reactions[10] or in certain solvent mixtures,[11] but direct displacements with alkali metal carboxylate fail. It also was reported[7] that $R_fCH_2CH_2OH$ could be made from the iodide by chemical oxidation under hydrolytic conditions with several different oxidizing agents.[12-14]

We have explored electrochemical reactions of (perfluoroalkyl)ethyl iodides under different conditions, and in this paper we report our results on the use of electrochemical oxidation to directly convert the iodides to the corresponding amides, esters, alcohols, and ethers in nonaqueous media under ambient conditions.

Most of the electrochemical studies of alkyl halides are confined to their reductions and anodic oxidations have received much less attention.[15] The only report on electrochemical oxidation of polyfluoroalkyl halides that we are aware of is the anodic oxidation of R_fI, $I(CF_2)_4I$, and $C_6F_{13}CH_2CH_2I$ in perfluoroalkanesulfonic acids (R'_fSO_3H) and fluorosulfonic acid (FSO_3H) to give polyfluorinated sulfonic ester (for example, $R_fSO_3R'_f$) and fluorosulfate (for example, R_fSO_3F) products.[16] Hydrolysis of the sulfonates is not straightforward, however. For instance, $C_6F_{13}CH_2CH_2OSO_2CF_3$ reportedly gives a mixture of an alcohol, olefin, and ether in about a 1:1:1 ratio.

Scheme I



Results and Discussion

We have measured anodic peak potentials of the perfluorinated and partially fluorinated alkyl iodides, R_fI and $R_fCH_2CH_2I$ where $R_f = C_6F_{13}$, C_8F_{17}, and $C_{10}F_{21}$, by cyclic voltammetry at various sweep rates (Table I). All the compounds showed one irreversible oxidation wave in the range of 1.39 to 2.15 V. The relatively small variations in the peak potentials with scan rates indicate that the electrochemical process is not diffusion controlled but is most likely followed by a fast chemical reaction within the scanning time domain. Interestingly, $C_8F_{17}CH_2CH_2I$ has the lowest anodic peak potential in the series. Although the anodic peak potentials of C_4F_9I and $C_6F_{13}I$ were very similar to that of $C_6F_{13}CH_2CH_2I$, attempts to carry out controlled potential electrolysis with the perfluoroalkyl iodides in acetonitrile failed because rapid and severe filming of the anode (platinum or glassy carbon) led to a drastic and immediate decrease in anodic current. An arbitrary increase of the applied anodic potentials up to +2.2 V (vs Ag wire) or frequent pulses of potentials as negative as −2.2 V on the anode did not increase the anodic current sufficiently to permit preparative-scale electrosyntheses. On the other hand, $R_fCH_2CH_2I$ could be oxidized preparatively to yield characterizable products in meaningful yields if potentials higher than their anodic peak potentials (for example, above 2 V) were applied. These observations may indicate that although filming occurs with both series of iodides, films from $R_fCH_2CH_2I$ are more soluble and more readily detached from the anode than those from R_fI when relatively high anodic potentials are applied.

We have selected $C_8F_{17}CH_2CH_2I$ to survey its utility in preparative electrosynthesis because, unlike its higher homologues, it is soluble in a variety of solvents and its products are less volatile and easier to isolate than those from its lower homologues. We found that the iodide could be directly transformed to a variety of products. Scheme I indicates the main types of products and illustrates the versatility of the anodic process. In the surveys, the electrolyses were typically carried out potentiostatically in an "H" type divided cell using 0.5 mmol of the iodide. The electrochemical conditions surveyed are summarized in Tables II–IV together with the amounts of organic products recovered and distributions of products.

Formation of Amides. The direct electrochemical conversion of $C_8F_{17}CH_2CH_2I$ in acetonitrile to $C_8F_{17}CH_2CH_2NHCOCH_3$ (**1**) was investigated by using different anode materials (Pt, graphite (C), and glassy carbon (GC)) with weakly nucleophilic (BF_4^-, ClO_4^-, HSO_4^-, and *p*-$CH_3C_6H_4SO_3^-$) salts as supporting electrolytes. The reaction proceeded either as a one-electron or a two-electron process and the results are summarized in Table II.

As shown in the first four entries, amide **1** constituted 40–45% of the product mixture when a platinum anode was used in conjunction with either tetrafluoroborate or perchlorate electrolytes. In a nondivided cell (entry 2), an iodinated amide, $C_8F_{17}CH(I)CH_2NHCOCH_3$ (**2**), was produced in 28% yield in addition to **1** (43%). With perchlorate salts (entries 3 and 4) another product was formed,

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(7) Brace, N. O. *J. Fluorine Chem.* **1986**, *31*, 151.

(8) Knell, M.; Klemchuck, P. U.S. Patent 3 671 574 (to Ciba Geigy Corp.), June 20, 1972; *Chem. Abstr.* **1972**, *77*, 4960a; 164049p.

(9) Knell, M.; Berger, E. U.S. Patent 3 686 281 (to Ciba-Geigy Corp.), August 22, 1972.

(10) Hayashi, T.; Yamaguchi, H. Jap. Patent 73 30 611 (to Asahi Glass Co.), November, 1973; *Chem. Abstr.* **1974**, *80*, 26771d.

(11) (a) Matsuo, M.; Yamaguchi, H.; Hayashi, T. *Asahi Garasu Kenkyu Hokoku* **1973**, *23* (2), 135; *Chem. Abstr.* **1974**, *81*, 104480v; presented in part at the 10th International Symposium on Fluorine Chemistry (10th ISFC), Vancouver, BC, Canada; August 1–6, 1982, Abstract 0-19, and at the 11th ISFC, East Berlin, August 5–9, 1985, Abstract C-6. (b) Hayashi, T.; Matsuo, M. Ger. Offen. DE 2 318 941 (to Asahi Glass Co. Ltd.), October 25, 1973; *Chem. Abstr.* **1974**, *80*(1), 14564a.

(12) MacDonald, T. L.; Narasimhan, N.; Burka, L. T. *J. Am. Chem. Soc.* **1980**, *102*, 7760.

(13) (a) Cambie, R. C.; Lindsay, B. G.; Rutledge, P. S.; Woodgate, P. D. *J. Chem. Soc., Chem. Commun.* **1978**, 919. (b) Cambie, R. C.; Chambers, D.; Lindsay, B. G.; Rutledge, P. S.; Woodgate, P. D. *J. Chem. Soc. Perkin Trans. 1* **1980**, 822. (c) Reich, H. J.; Peake, S. L. *J. Am. Chem. Soc.* **1978**, *100*, 4888. (d) Ogata, K.; Aoki, K. *J. Org. Chem.* **1969**, *34*, 3974 and 3978.

(14) von Werner, K. Ger. Offen. DE 3 035 641 (to Farbwerke Hoechst A.-G.), May 6, 1982; *Chem. Abstr.* **1982**, *97*, 91725g.

(15) (a) Becker, J. Y. *Electrochemical Oxidation, Formation and Reduction of the C-X Bond-Direct and Indirect Processes in The Chemistry of the Functional Groups*; Patai, S., Ed., Supplement D; *The Chemistry of Halide, Pseudohalides, and Azides*; Patai, S., Rappoport, Z., Eds.; Wiley and Sons: New York, 1983; pp 203–286. (b) For electrochemical reduction, see, e.g.: Benefice-Malouet, S.; Blancou, H.; Calas, P.; Commeyras, A. *J. Fluorine Chem.* **1988**, *39*, 125.

(16) Germain, A.; Commeyras, A. *Tetrahedron* **1981**, *37*, 487.

Table II. Anodic Oxidation of $C_8F_{17}CH_2CH_2I$ in Acetonitrile To Form Amides—Experimental Data and Product Distribution[a]

					X in $C_8F_{17}CH_2CH_2X$ (% by GLC)			
entry	anode[b]/ *E* (V)	electrolyte[c] (0.1 M)	product mixture, mg	F/mol	I	OH	NHCOCH$_3$	notes
1	Pt/2.3	TBAF	120	2.2	30		40	*n*-Bu$_3$N (30)
2[d]	Pt/2.4	TBAF	150	2.0	29		43	**2** (28)
3	Pt/2.2	LiClO$_4$	220	2.2			40	**3** (60)
4	Pt/2.3	TBAClO$_4$	140	1.5			40	**3** (60)
5	Pt/2.4	TEAOTs[e]	160	1.5	99		0	
6	Pt/2.3	TBAHSO$_4$[f]	140	1.2	95	5		
7	Pt/2.2	ClSO$_3$H/Et$_3$N	75[g]	5.0	0		75	unidentified (25%, *m/z* 113)
8	C/2.2	TEAF	100	1.85	50	1–2	46	
9	C/2.1	TBAClO$_4$	100	3.3			40	**3** (60)
10	C/2.1	LiClO$_4$	70	4.0			55	**3** (45)
11	GC/2.3	TBAF	200	1.9			75	*n*-Bu$_3$N (25)
12	GC/2.3	TBAClO$_4$	100	1.75			43	**3** (57)
13[h]	GC/2.3	TBAF	750	1.4	33		67	isolated by column chromatography
14[h]	GC/2.3	TBAF	470	2.2			70	*n*-Bu$_3$N (30)
15	Pt/2.3	TBAF–10% crotonitrile	930	1.1	30		26	**5** (7)[i]
16	Pt/2.3	TBAF–10% methacrylonitrile	1600	2.3			*j*	
17	Pt/2.3	TBAF–10% methacrylonitrile in CH$_3$NO$_2$	520	2.3				**6** (40)[k]

[a] Electrolyses were carried out potentiostatically in an "H" type divided cell using 0.5 mmol (287 mg) of $C_8F_{17}CH_2CH_2I$ in 30 mL of 0.1 M electrolyte solution in acetonitrile, unless otherwise stated. The quoted applied potentials are vs Ag wire quasi-reference electrode. [b] C = graphite and GC = glassy carbon. [c] TBAF = *n*-Bu$_4$BF$_4$ and TEAF = Et$_4$BF$_4$. [d] Nondivided cell. [e] Five pipet drops of trifluoroacetic anhydride (TFA$_2$O) were added to the anolyte solution. [f] Electrolyte was dried at 150 °C for a few hours before being used. [g] Actually 550 mg were isolated after the usual workup (see Experimental Section). Upon washing with 5% HCl, only 75 mg of products remained. It seems that the washed stuff contained inorganic materials. [h] 1.5 mmol of $C_8F_{17}CH_2CH_2I$ was ued. [i] The rest consists of dimer, trimers, and oligomers composed of crotononitrile and acetonitrile as evidenced by GC/MS. [j] Product mixture contains starting material, *n*-Bu$_3$N, and trimers and oligomers composed of methacrylonitrile and acetonitrile as evidenced by GC/MS. [k] The rest contains *n*-Bu$_3$N and dimers and trimers between methacrylonitrile and nitromethane as evidenced by GC/MS.

which, according to its spectroscopic properties (^{1}H NMR, IR) and elemental analysis (for C, H, Cl), corresponded to a solvated, covalently bound organic perchlorate, $C_8F_{17}CH_2CH_2OClO_3\cdot CH_3CN$ (**3**). The nature of the electrolyte cation (Li$^+$ and TBA$^+$) had no effect (entries 3 and 4). Organic perchlorates have been prepared previously by chemical oxidative deiodination of alkyl iodides in the presence of perchlorate salts and are reported to be relatively stable.[17]

With a mixture of chlorosulfuric acid and triethylamine as the electrolyte (entry 7), the relative yield of 1 remained high (75%), but the product recovery (75 mg) and current efficiency (5 F/mol) were significantly reduced. With tetraethylammonium (TEA) tosylate or TBA hydrogen sulfate (entries 5 and 6), the anodic process became totally inefficient. In these cases, most of the electricity apparently was consumed by the oxidation of water in the highly hygroscopic electrolytes, although addition of trifluoroacetic anhydride to the electrolytic solution or preheating of the electrolyte in vacuum had little effect. Alcohol $C_8F_{17}CH_2CH_2OH$ (4) obtained in small amounts in entries 6 and 8 could have been generated either by hydrolysis of an ester intermediate (e.g., $C_8F_{17}CH_2CH_2OSO_3H$) or by a reaction of the cation radical of the iodide with water.

On graphite anodes (entries 8–10) the relative yield of amide 1 was moderate (40–55%), although the amount of electricity consumed increased from 1.8 to 4 F/mol. In the presence of perchlorate salts, compound 3 again was formed and anode materials appear to have little effect on the relative yield of 3 (entries 3, 4, 9, 10, and 12). With TBABF$_4$ (entry 11), however, the relative yield of amide 1 increased to 75% and the electricity consumption remained less than 2 F/mol. In larger scale reactions (entries 13 and 14), the relative yields of amide 1 were similar (~70%) at both 1.4 and 2.2 F/mol consumption, although in the latter case no starting material remained. Thus, the results strongly suggest that polymeric or volatile products were also formed either by direct oxidation of the starting iodide or by further oxidation of amide 1.

Attempts to prepare the unsaturated carboxylic acid amides, $C_8F_{17}CH_2CH_2NHCOCH{=}CHCH_3$ (**5**) and $C_8F_{17}CH_2CH_2NHCOC(Me){=}CH_2$ (**6**), in the presence of crotononitrile and methacrylonitrile, respectively, were less successful. The relative yield of **5** was 7% and the rest of the product consisted of 1 (26%) and oligomers of crotononitrile (entry 15). Under similar conditions but with methacrylonitrile, no amide was formed (entry 16). However, when this reaction was carried out in nitromethane (entry 17), **6** constituted 40% of the product mixture, which also contained tributylamine and condensation products of methacrylonitrile with nitromethane. Tributylamine found in some anolytes is most likely derived from TBA cations by cathodic reduction followed by migration to the anode compartment.

Formation of Esters. In attempts to expand the scope of the anodic oxidation of $C_8F_{17}CH_2CH_2I$, other weak nucleophiles were also examined. Surprisingly, the reaction in acetonitrile in the presence of trifluoroacetate (TFA) salts afforded the trifluoroacetate ester, $C_8F_{17}CH_2CH_2OCOCF_3$ (**7**), in good yields (Table III). This reaction was reasonably efficient if the oxidation was carried out on Pt anode in a divided cell. Effective electrolytes included TFANa (entry 1), a mixture of TFANa and tetraethylammonium tetrafluoroborate (TEAF) (entry 6), and a mixture of trifluoroacetic acid and triethylamine (entry 7). With the latter as the supporting electrolyte, a trace amount of alcohol **4** was detected, which became more noticeable when this reaction was scaled-up (entry 8). This alcohol was also detected when a single cell was used, but the transformation to the trifluoroacetate ester **7** was less efficient (entry 2), probably due to reduction of the starting iodide in a single cell. In the presence of 2% water, water apparently was preferentially oxidized and most of the starting material was recovered (entry 3). Similarly, the lower yield of ester **7** in entry 4 may be attributed to the high hygroscopicity of ammonium trifluoroacetate.

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(17) Zefirov, N. S.; Zhdankin, V. V.; Koz'min, A. S. *Tetrahedron Lett.* **1986**, *27*, 1845. Zefirov, N. S.; Zhdankin, V. V.; Makhon'kova, G. V.; Dan'kov, Y. V.; Koz'min, A. S. *J. Org. Chem.* **1985**, *50*, 1872 and references therein.

Table III. Anodic Oxidation of $C_8F_{17}CH_2CH_2I$ To Form Esters and Diesters[a]

						X in $C_8F_{17}CH_2CH_2X$ (% by GLC)				
entry	anode/ *E* (V)	solvent (mL anolyte)	electrolyte (0.1 M)	product mixture, mg	*F*/mol	I	OH	$NHCOCH_3$	ester	notes
1	Pt/2.4	CH_3CN (30)	TFANa	160	1.8	15			**7** (85)	*b*
2	Pt/2.4	CH_3CN (50)	TFANa	150	2.6	77	3		**7** (20)	*b*, *c*
3	Pt/2.3	2% H_2O–CH_3CN (30)	TFANa	110	2.8	98			**7** (2)	
4	Pt/2.4	CH_3CN (30)	$TFANH_4$	110	1.4	70		trace	**7** (30)	*b*
5	C/2.2	CH_3CN (30)	TFANa	230	2.2	48	1–2		**7** (50)	*b*
6	Pt/2.3	CH_3CN (30)	TEAF + TFANa (1:1), 0.05 M each	160	2.2	10			**7** (90)	*b*
7	Pt/2.4	CH_3CN (30)	TFA (0.1), Et_3N (0.1)	110	3.0	7	trace		**7** (93)	*b*
8[d]	Pt/2.3	CH_3CN (100)	TFA (0.1), Et_3N (0.1)	530	3.0	13.5	3.5		**7** (83)	
9[e]	Pt/2.25	CH_3CN (100)	TFANa (0.05), TEAF (0.05)	800	2.25		7	18	**7** (75)	*f*
10	Pt/2.3	CH_3CN (30)	CCl_3COONa	80	0.8	99		0	0	*g*
11	Pt/2.2	20% HOAc/CH_3CN (30)	AcONa	140	1.95	86			**8** (14)	*h*
12	Pt/1.9	CH_3CN (30)	TBAOAc (0.08)	40	1.8	trace			**8** (75)	*n*-Bu_3N, *n*-BuI
13	Pt/2.3	CH_3CN (30)	TBAOBz (0.05)	100	1.6	24	trace		**9** (76)	
14	Pt/2.5	CH_3CN (30)	TEAF (0.05), Et_3N + excess of $CH_2{=}CHCOOH$ (0.05/0.15)	100	4.0	4		89	**10** (5)	
15	Pt/2.5	CH_3CN (30)	Et_3N (0.15), $CH_2{=}CHCOOH$ (0.05), TEAF (0.05)	100	4.0	3.5		89.5	**10** (5)	
16	Pt/2.3	CH_3CN (30)	TEA acrylate (0.05)	90	2.3		7		**10** (7)	mostly *n*-Bu_3N
17	GC/2.3	CH_3CN (30)	TEA acrylate	90	2.3		3			mostly *n*-Bu_3N
18	C/2.4	CH_3CN (30)	TBAOAc (0.05) + TEAF (0.05) + 2 mL acrylic acid	220	1.6	50		40	**10** (10)	
19	Pt/2.45	CH_3CN (30)	TEAF (0.05), Et_3N (0.05), $CH_2{=}C(Me)COOH$ (0.8)	70	4.65	41		50	**11** (9)	
20	Pt/2.3	CH_3CH (30)	$CH_2{=}C(Me)COOH$ (0.12), TEAF (0.05), Et_3N (0.05)	130	2.3	70			**11** (25)	
21	Pt/2.4	CH_3CN (30)	TEAF (0.05), Et_3N + excess $CH_2{=}C(Me)COOH$ (1:16)	70	4.6	54	8	38		
22	Pt/2.3	CH_3CN (30)	TBA(methacrylate)·$(H_2O)_n$	80	2.52	0			**11** (15–20)	isolated yield
23	GC/2.3	CH_3CN (30)	TBAF (0.05) TBA(methacrylate)·$(H_2O)_n$ (0.05)	70	2.2		(rest is TBA)		**11** (25)	*n*-Bu_3N (75)
24	Pt/2.3	CH_3CN (30)	TBA(methacrylate)·$(C_6H_6)_n$ (0.5)	60	2.0				**11** (63)	*n*-Bu_3N + unidentified (*m*/*z* 560)

	oxidation of $(CF_2CH_2CH_2I)_2$								
entry	anode/ *E* (V)	solvent (mL anolyte)	electrolyte (0.1 M)	product mixture, mg	*F*/mol	iodide	monoester	diester	notes
25	Pt/2.4	CH_3CN (30)	TFANa (0.1)	90	4.4		**12** (1)	**13** (99)	*b*
26	Pt/2.1	CH_3CN (30)	TFANa (0.1)	150	2.1	31	**12** (9)	**13** (60)	*b*, *i*
27	GC/1.8	CH_3CN (30)	TFANa (0.05), TEAF (0.05)	180	2.1	30	**12** (38)	**13** (25)	*b*, *j*

[a] See footnotes *a*, *b*, and *c* of Table II for electrolysis conditions. [b] Five pipet drops of TFA_2O were added to anolyte before electrolysis was initiated. [c] Nondivided cell. [d] 1.5 mmol of the iodide substrate was used. [f] 1.75 mmol of the iodide substrate was used. [f] As in (*b*) but 20 drops. [g] As in (*b*) but with $(CCl_3CO)_2O$. [h] As in (*b*) but with Ac_2O. [i] Trace of $ICH_2CH_2(CF_2)_2CH_2CH_2OH$ as evidenced by GC/MS. [j] Trace of $ICH_2CH_2(CF_2)_2CH_2CH_2NHCOCH_3$.

On graphite anode (entry 5) the process was less efficient because the anode itselt was oxidized at the relatively high anodic potentials and the surface was degraded during the electrolysis. On GC anode severe and immediate filming by white solid occurred, which prevented further electrolysis.

Interestingly, we observed considerable migration of solution from the anode to the cathode compartment when TFANa was used as the sole supporting electrolyte. The migration was considerably less with a Et_3N–trifluoroacetic acid (entry 7) or TFANa–TEAF mixture (entry 6). This reaction was scaled-up under two different conditions. In the presence of the mixed TFANa–TEAF electrolyte (entry 9), the relative yield of ester **7** remained high (75%) but amide **1** (18%) and alcohol **4** (7%) were also formed. However, with TFA–Et_3N (entry 8) no amide **1** was detected and the relative yield of **7** was high (83%), although 13.5% of the starting iodide remained even after 3 F/mol of electricity was consumed. By contrast, with sodium trichloroacetate as the supporting electrolyte (entry 10), no more than 0.8 F/mol of electricity could be passed through. In this case the recovery was low and only the starting material was detected in the reaction mixture by GLC.

Under carefully controlled conditions, the trifluoroacetate ester **7** can be readily and quantitatively hydrolyzed to alcohol **4** without yielding any detectable amounts of olefin, $C_8F_{17}CH{=}CH_2$.

$$\underset{\mathbf{7}}{C_8F_{17}CH_2CH_2OCOCF_3} \xrightarrow[\text{10–15 min at room temperature}]{\text{2\% Et}_3\text{N, MeOH–H}_2\text{O (1:1)}} \underset{\mathbf{4}}{C_8F_{17}CH_2CH_2OH}$$

With sodium acetate (entry 11) as the electrolyte, the corresponding acetate ester, $C_8F_{17}CH_2CH_2OCOCH_3$ (**8**), was obtained but the yield was considerably lower than that achieved in the trifluoroacetate ester (**7**) synthesis. After about 2 F/mol of electricity was consumed, the reaction mixture was mostly the starting material. When the counter-cation was changed to TBA and the applied potential was reduced from 2.2 to 1.9 V (entry 12), most of the starting material was consumed and the desired ester (**8**) was produced, but the yield was low. With TBA benzoate (entry 13), the corresponding benzoate ester, $C_8F_{17}CH_2CH_2OCOC_6H_5$ (**9**),[18] was obtained in good yield similar to that achieved in the trifluoroacetate ester synthesis. The significant difference between the low ester yields with the acetate anion and the relatively high yields with the trifluoroacetate and benzoate anions cannot be accounted for by the difference in the nucleophilicity of the anions. We suggest that, under the reaction conditions, anodic decarboxylation of the acetate anion competes with oxidation of the iodide, whereas the TFA and benzoate anions are more difficult to oxidize and, consequently, the current efficiency and yields were much higher for **7** and **8**.

Preparation of the acrylate ester, $C_8F_{17}CH_2CH_2OCOCH{=}CH_2$ (**10**),[19] also was investigated under different conditions (entries 14–18). The relative yields of **10** were only 5–10% and the amide **1** was the major product when the oxidation was carried out on Pt (entries 14 and 15) or C (entry 18) anodes. With GC anode, **10** was not formed at all (entry 17), but small amounts of alcohol **4** (3–7% relative yield) were detected with both Pt and GC anodes when TEA acrylate was used as the electrolyte (entries 16 and 17).

Attempts were also made to directly obtain the methacrylic ester, $C_8F_{17}CH_2CH_2OCOC(Me){=}CH_2$ (**11**), and results are shown in Table III (entries 19–24). Under the conditions that gave the trifluoroacetate **7** in high yields (entries 6 and 7), the methacrylate **11** was generated only in low yields (9–25%, entries 19 and 20), which nevertheless were higher than those realized for **10**. Addition of excess of methacrylic acid (entry 21) did not improve the yield. In the first two entries, 19 and 20, the major product was the amide **1** but in all three cases considerable amounts of the starting material were still present, even after 2.3–4.6 F/mol of electricity was consumed. This observation strongly suggests that the oxidation of the methacrylate anion competes with that of the iodide. The poor current efficiency was hardly affected by changing the counter-cation, TEA or TBA, or the anode material, Pt (entry 22) or GC (entry 23). Interestingly, when benzene-washed TBA methacrylate instead of the hydrated salt was used (entry 24), the relative yield of **11** increased to 60%, although the total product yield still remained low. This result implies that even if water, which could compete with the iodide for oxidation, is removed, preferential oxidation of methacrylate anion still cannot be avoided.

Formation of Diesters. The anodic oxidation of a diiodo derivative, $(CF_2CH_2CH_2I)_2$, and its conversion to the mono- and bis(trifluoroacetic ester), $ICH_2CH_2(CF_2)_2CH_2CH_2OCOCF_3$ (**12**) and $(CF_2CH_2CH_2OCOCF_3)_2$ (**13**), are described in the last three entries in Table III. When the anode was Pt and 4.7 F/mol of electricity was consumed, the product consisted almost entirely of the diester **13** (entry 25). Interestingly, when 2 F/mol was passed through, the ratio of **12**:**13** was approximately 1:6. This ratio indicates that the anodic substitution of the second iodide functionality is faster than that of the first. It would seem that the ester functionality in compound **12** is too remote from the C–I bond to have any significant electronic effect on its rate of oxidative cleavage. Also, it is difficult to envision any reasonable cyclic interaction between the terminal ester and iodide groups that might enhance oxidative cleavage. Although the origin of this behavior remains unclear, specific adsorption of the substrate on the anode surface may be responsible for the observed result. In fact, when the anode material was changed from Pt to GC, the ratio changed to approximately 2:3 in favor of the monoester **12** at 2 F/mol of electricity consumption (entry 27 in Table III). Obviously, the anode material plays an important role in the electrochemical activation of the C–I bond in the diiodide substrate and the monoester **12**.

Formation of Ethers. The anodic oxidation of $C_8F_{17}CH_2CH_2I$ apparently does not compete with that of methanol, since no products were detected in this solvent, even after passing 4–8 F/mol of electricity (Table IV, entries 1–3). Neither the anode material nor the nature of the electrolytes affected the reaction. However, when the electrochemically inert 2,2,2-trifluoroethanol was used as the electrolytic solvent, several products were formed and their relative yields were highly dependent on the nature of both anodic material and electrolyte. In the presence of $TBABF_4$ with a Pt anode, a moderate amount (100 mg) of products was obtained after 1.8 F/mol was consumed (entry 4). The product mixture consisted of the starting material and four other compounds, $C_8F_{17}CH_2CH_2OCH_2CF_3$ (**14**), $C_8F_{17}CH(I)CH_2OCH_2CF_3$ (**15**), $C_8F_{17}CH(I)CH_3$ (**16**), and alcohol **4**. When the amount of electricity was increased to 2.5 F/mol (entry 5) in an attempt to oxidize all of the starting material, the material balance decreased significantly (40 mg) and the product mixture contained only **14**, but the starting material was still present. When the Pt anode was replaced by GC and 2.2 F/mol of electricity was passed (entry 6), ethers **14** and **15** were formed, but the starting material was the major component of the product mixture. With the graphite anode, the current did not decay in the "usual" manner. When the electrolysis was arbitrarily stopped after the consumption of 6.3 F/mol

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[18] Fasick, R. W. U.S. Patent 3 239 557 (to E. I. du Pont de Nemours & Co.), March 8, 1966; *Chem. Abstr.* **1966**, *64*, 14098c.

[19] Jaeger, H. Ger. Offen. DE 2 311 277 (to Ciba-Geigy A.-G.), September 27, 1973; *Chem. Abstr.* **1973**, *79* (25), 146014k. Maruyama, T.; Yokoo, H. Jpn. Kokai Tokyo Koho JP 61/180743 A2 [86/180743] (to Showa Rhodia Kagaku Co., Ltd.), August 13, 1986; *Chem. Abstr.* **1986**, *106* (16), 120363z.

Table IV. Oxidation of $C_8F_{17}CH_2CH_2I$ in Alcohols—Experimental Data and Product Distribution[a]

entry	anode/ *E* (V)	solvent	electrolyte (0.1 M)	product mixture, mg	*F*/mol	products (% by GLC)
1	Pt/2.1	CH_3OH[b]	TBAF	110	4.1	only starting material (s.m.)
2	GC/2.0	CH_3OH[b]	TBAF	140	4.0	only s.m.
3	GC/2.1	CH_3OH[b]	TEAOTs	150	8.0	only s.m.
4	Pt/2.2	CF_3CH_2OH	TBAF	100	1.8	s.m. (23); **14** (38); **15** (20); **4** (10); **16** (8)
5	Pt/2.2	CF_3CH_2OH	TBAF	40	2.5	s.m. (35); **14** (65)
6	GC/2.2	CF_3CH_2OH	TBAF	100	2.2	s.m. (60); **14** (36); **15** (2); 2% unknown
7	C/2.2–1.9[c]	CF_3CH_2OH	TBAF	70	6.3	**14** (80); **17** (12); **4** (6); **15** (1)
8	Pt/2.2	CF_3CH_2OH	$TBAClO_4$	90	2.8	trace of s.m.; **18** (55); **14** (30); **15** (7)
9	GC/2.2	CF_3CH_2OH	$TBAClO_4$	140	4.0	**14** (47); **4** (42); **18** (11)
10	GC/2.2	CF_3CH_2OH/ CH_3CN (1:1)	$TBAClO_4$	190	2.9	**1** (30); **14** (30); **18** (40)
11	GC/2.2	CF_3CH_2OH/ CH_3CN (9:1)	$TBAClO_4$	160	2.8	**1** (40); **14** (15); **18** (45)
12	GC/2.4	CF_3CH_2OH/ CH_3CN (1:1)	TBAF	180	4.0	**14** (24); **1** (33); **19** (40); + others
13	GC/2.1	CH_3CN/ CF_3CH_2OH (9:1)	TBAF	130	3.1	**14** (58); **1** (31); **19** (7); **4** (1); + others

[a] See footnotes *a*, *b*, and *c* of Table II for electrolysis conditions. [b] Distilled over CaH_2. [c] The initial applied potential was 2.2 V and it was gradually decreased to 1.9 V due to overloading.

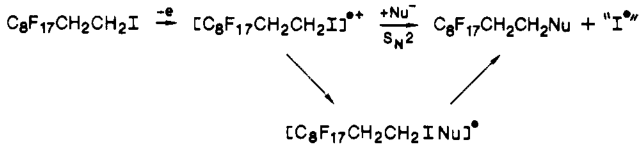
(entry 7), a small amount (70 mg) of products was recovered, which consisted mainly of **14** and smaller amounts of **15**, **17**, and alcohol **4**. The new ether product, $C_8F_{17}CH(OCH_2CF_3)CH_3$ (**17**), was found only with the graphite anode.

When $TBABF_4$ was substituted by $TBAClO_4$ (entries 8 and 9), the starting material was almost totally consumed after only 2.8 F/mol of electricity was passed through and, in addition to **14** and **15** (on Pt anode) or **14**, **15**, and alcohol **4** (on GC anode) a new product emerged. The "new" product exhibited chemical properties very similar to those of the covalent perchlorate **3** that we observed earlier, and its spectral properties are consistent with a trifluoroethanol-solvated perchlorate, $C_8F_{17}CH_2CH_2OClO_3{\cdot}CF_3CH_2OH$ (**18**).

To examine the effect of mixed solvents on the anodic process, we oxidized the iodide in a 1:1 mixture of CH_3CN/CF_3CH_2OH in the presence of $TBAClO_4$ (entry 10). The amount of the recovered products was high (190 mg), with **18** as the major product and about equal but smaller amounts of amide **1** and ether **14**. Upon increasing the amount of acetonitrile in the solvent mixture (entry 11), the relative amount of amide **1** increased as expected but mostly at the expense of the alcohol **4**, and the relative yield of **18** essentially remained unchanged. When $TBAClO_4$ was substituted by $TBABF_4$ (entries 12 and 13), the product ratio **1**/**14** in a given solvent mixture changed only slightly. However, instead of the covalent perchlorate **18**, an iminoether, $C_8F_{17}CH_2CH_2N{=}C(OCH_2CF_3)CH_3$ (**19**), constituted 31–40% of the product mixture. This result suggests that the iminium cation, $[C_8F_{17}CH_2CH_2N{\equiv}CCH_3]^+$, can be trapped by trifluoroethanol.

Mechanism. The results discussed above show that the iodine of $R_fCH_2CH_2I$ can be replaced by the acyloxy, OH, OCH_2CF_3, or $NHCOCH_3$ groups. It is unlikely that the substitution proceeds via a S_N1 type mechanism, because the carbenium ion, $R_fCH_2CH_2^+$, is destabilized by the perfluoroalkyl group[20] and is likely to undergo immediate proton elimination to form olefin. We postulate that the radical cation, $R_fCH_2CH_2I^{\bullet+}$, directly reacts with nucleophiles either to displace "I•" via an S_N2 type process or, more likely, to form a hypervalent iodanyl radical intermediate which could collapse to give the carbon substitution products and "I•" (Scheme II). The latter mechanism involving the hypervalent intermediate is consistent both with the results of this study in that the substitution reaction proceeds best with nucleophiles that stabilize hypervalent bonds and with the earlier observation[21] that the anodic oxidation of optically active 2-iodooctane proceeds with 80% retention of configuration. The formation of traces of $C_8F_{17}CH{=}CH_2$, however, cannot be entirely ruled out since its polymerization could have caused the anode filming. Furthermore, although the majority of the products had a functional group at the terminal carbon, minor products (**15**, **16**, and **17**) having a substituent at the internal carbon were also formed, which might have arisen by addition of HI or CF_3CH_2OH to the olefin.

Scheme II



Scheme III

$$0.5I_2 \text{ (or “I•”)} - e \rightarrow \text{“}I^+\text{”}$$
$$\text{“}I^+\text{”} + R_fCH_2CH_2I \rightarrow [R_fCH_2CH_2I]^{\bullet+} + 0.5I_2 \text{ (or “I•”)}$$

As to the fate of iodine, we observed the formation of I_2 when CF_3CH_2OH was used as the electrolysis solvent. At the relatively high anodic potentials used in these oxidations, positively charged iodine species may be formed as suggested for the anodic oxidation of alkyl iodides.[16,22] The fact that in most of the preparative-scale electrolyses of $C_8F_{17}CH_2CH_2I$ more than 1 F/mol of electricity was consumed suggests that electricity was also used to oxidize $I^\bullet$ or I_2. Should this be the case, one cannot rule out the possibility that positively charged iodine species (for example, I^+, I_2^+, I_3^+)[23] are also involved in an indirect oxidation of $R_fCH_2CH_2I$ by homogeneous electron transfer (Scheme III).

Conclusions

Our survey of oxidative electrochemical reactions of polyfluoroalkyl iodides, $R_fCH_2CH_2I$, reveals that the iodide ($R_f = C_8F_{17}$) can be directly converted in good yields to the corresponding acetamide **1**, trifluoroacetate **7**, and

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[20] Olah, G. A.; Mo, Y. K. In *Advances in Fluorine Chemistry*; Tatlow, J. C., Peacock, R. D., Hyman, H. H., Eds.; Butterworth: London, 1973; Vol. 7, p 69.

[21] Laurent, A.; Laurent, E.; Tardivel, R. *Tetrahedron* **1974**, *30*, 3423 and 3431.

[22] Miller, L. L.; Watkins, B. F. *Tetrahedron Lett.* **1974**, 4495.

[23] Adhami, G.; Herlem, M. *J. Electroanal. Chem.* **1970**, *26*, 363.

benzoate **9**. The direct anodic transformations to ethers and other amides and esters, however, proceed only in moderate to poor yields. The results can be accounted for by a mechanism that involves a hypervalent iodanyl radical species as a critical intermediate. The trifluoroacetate ester **7** can be hydrolyzed quantitatively to alcohol **4** without yielding any detectable amounts of elimination products.

Experimental Section

Cyclic voltammetry measurements were carried out with a Princeton Applied Research (PAR) potentiostat Model 173 and PAR Universal Programmer Model 175. The voltammograms were recorded on a PAR xy-recorder Model RE0091. All measurements were done on Pt working electrode and peak potentials were quoted vs Ag wire quasi-reference electrode. Preparative-scale electrosyntheses were performed in an "H" type cell using the potentiostat coupled with a PAR Digital coulometer plug-in unit Model 179. The details of the cells size and construction were described elsewhere.[24]

Gas chromatographic analyses were carried out on Hewlett Packard Model 5790 chromatograph with a thermal conductivity detector using a 6 × $^1/_2$ ft 10% SP-2100 on an 80–100-mesh Supelcoport column and programmed at 100 °C for 3 min and to 180 °C at 30 °C/min.

A pure sample of $C_8F_{17}CH_2CH_2I$ was purchased from Fluorochem Ltd. and other fluoro iodides were available in our laboratories. The electrolytes, n-Bu_4NBF_4, $LiClO_4$, n-Bu_4NClO_4, Et_4NBF_4, Et_4N(tosylate), CF_3COONa, CH_3COONa, CF_3COONH_4, CCl_3COONa, and n-Bu_4NHSO_4 were purchased (Aldrich) and used without further purification unless specified otherwise. Acetonitrile was HPLC grade (Fisher Co.) and was either used without further purification or distilled over P_2O_5 immediately before use. Methanol was distilled over CaH_2 and CF_3CH_2OH (Eastman Kodak) was used without further purification.

Tetrabutylammonium Carboxylates. Tetrabutylammonium (TBA) salts of acrylate, methacrylate, acetate, and benzoate, were prepared from commercially available (Aldrich) TBA hydroxide solutions (40% in water or 1 M in methanol). Typically, 30 mL (0.0462 mol) of the base solution was added to a round-bottomed flask containing an equimolar amount of the acid and the mixture was stirred for 1 h under a nitrogen atmosphere. The product was extracted with dichloromethane, and the combined organic extracts were washed twice with water, dried over $MgSO_4$, and filtered. Evaporation of the solvent usually afforded a colorless oil, which, in some cases, contained molecules of solvation and/or free acid. To remove as much water or methanol as possible from the TBA carboxylates, the oily product was azeotroped with benzene and then evaporated. The ^1H NMR spectrum of the residue showed that benzene molecules had replaced the solvated water or methanol molecules.

***N*-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluoro-*n*-decyl)acetamide (1).** A solution of 1.7 g (0.1 mol) of n-Bu_4NBF_4 (recrystallized from ethyl acetate–hexane) in 50 mL of CH_3CN (distilled over P_2O_5) was placed in an "H" type cell (3:2 in volume). A glassy carbon (2 × 2 cm) plate was used as the working anode. The background current at 2.3 V was 4 mA. To the anolyte compartment containing 30 mL of the solution was added 287 mg (0.5 mmol) of $C_8F_{17}CH_2CH_2I$, whereupon the current increased to 24 mA. The reaction was stopped after 95 C of electricity was consumed. Most of the solvent was evaporated from the anolyte mixture. The residue was taken up in water and extracted with diethyl ether. The combined organic extracts were dried over $MgSO_4$ and filtered. The solvent was evaporated to yield 200 mg of material consisting of 75% of **1** and 25% of n-Bu_3N by GC/MS and ^1H NMR analyses.

The reaction was scaled-up three fold. At controlled potential of 2.3 V, a solution of 861 mg of $C_8F_{17}CH_2CH_2I$ in 150 mL of the acetonitrile–electrolyte solution was oxidized. After similar workup and purification by column chromatography (100 g of silica gel eluted with 25% v/v acetone in hexane) followed by sublimation, amide **1** was isolated in 67% yield, mp 78–79 °C: ^1H NMR (δ, ppm) 1.99 (s, 3 H), 2.1–2.7 (m, 2 H), 3.60 (q, 2 H), 5.7–6.0 (NH); MS, m/z (relative intensity) 505 (M^+), 486, 482, 462, 424, 136, 119, 86, 72, 69, 43 (100). Anal. Calcd for $C_{12}H_8F_{17}NO$: C, 28.53; H, 1.60; F, 63.93. Found: C, 28.51; H, 1.52; F, 63.82.

(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluoro-*n*-decyl)trifluoroacetate (7). In a typical experiment, a solution of CF_3COOH (0.1 mol), Et_3N (0.1 mol), and 4 pipet drops of $(CF_3CO)_2O$ in 50 mL of CH_3CN (Fischer HPLC grade) was introduced in the open air into the two compartments (2:3 in volume) of an "H" type cell. Both electrodes were platinum screens (~6.5 cm^2). A controlled potential of 2.4 V (vs Ag wire) was applied to measure background current (3.1 mA). To the larger anodic compartment containing 30 mL of the solution was added 287 mg (0.5 mmol) of $C_8F_{17}CH_2CH_2I$ (i = ~15 mA), and continuous pulsing to 0 V was applied for 1 s every 10 s. The electrolysis was terminated after 152 C of electricity was consumed. Most of the solvent was evaporated from the anolyte mixture, and the residue was partitioned into 10% $NaHCO_3$ and Et_2O. The organic layer was washed twice with H_2O, dried over $MgSO_4$, and filtered. Evaporation of the solvent afforded 110 mg of product mixture, which consisted of starting material (7%) and **7** (93%) by GLC. **7**: ^1H NMR (δ, ppm) 2.6 (m, 2 H), 4.62 (t, 2 H); MS, m/z 560 (M^+), 447, 427, 377, 313, 191, 141, 115, 99, 95, 77, 69.

This reaction was scaled-up (×3.5) at a controlled potential of 2.25 V. Thus, from 1 g of $C_8F_{17}CH_2CH_2I$, 800 mg (84%) of the ester **7** was obtained after workup.

3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Hexadecafluoro-*n*-decyl 2,2,2-Trifluoroethyl Ether (14). Experiments were carried out on glassy carbon, platinum, or graphite anode under conditions similar to those described above except that the solvent was CF_3CH_2OH instead of CH_3CN: ^1H NMR (δ; ppm) 2.1–3.0 (m, 2 H), 3.90 (q, 2 H), 3.95 (t, 2 H); MS, m/z 545 (M − 1), 507, 477, 427, 377, 357, 313, 181, 169, 149, 131, 113, 95, 77, 61, 51; 546 (M^+, CI).

Spectral Data. ^1H NMR (δ ppm) and MS (m/z, relative intensity) of other products obtained from anodic oxidation of $R_fCH_2CH_2I$ ($R_f = C_8F_{17}$). **2**: 1.93 (s, 3 H), 3.50 (q, 2 H), 5.8 (NH), other signals are masked; 631 (M^+), 612, 504, 484, 462, 441, 423, 262, 127, 82, 72. **3**: 2.2–3.05 (m), 4.87 (t); 441, 169, 131, 113, 95, 77, 69, 65, 51. Anal. for C, H, Cl was satisfactory. IR spectrum gives absorption bands at 1030, 1105, 1150 and 1215 cm^{-1} for the perchlorate, and 2255 cm^{-1} for the nitrile. **4**[1,3,4,5b]: 4.03 (t, 2 H), 2.0–2.8 (m, 2 H); 465 (M^+), 444, 427, 405, 395, 195, 181, 169, 157, 145, 127, 113, 95, 69, 31 (100); 464 (CI, M^+). **5**: 2.15 (m, 3 H), 3.65 (q, 2 H), 5.39 (m, 1 H), 5.69 (m, 1 H), 6.1 (NH); 531 (M^+), 488, 186, 161, 120, 94, 81, 69, 41. **6**: 2.11 (m, 3 H), 2.1–2.7 (m, 2 H), 3.65 (t, 2 H), 5.15 (s), ~6 (NH); 531 (M^+), 512, 476, 254, 162, 142, 128, 98, 69, 41. **8**[11]: 2.11 (s, 3 H), 2.0–2.8 (m, 2 H), 4.35 (t, 2 H); 507 (M^+ + 1), 169, 131, 119, 100, 95, 87, 77, 73, 69, 55, 61, 51, 43 (100); 506 (CI, M^+). **9**: 2.1–3.0 (m, 2 H), 4.60 (t, 2 H), 7.45 (m, 3 H), 8.05 (m, 2 H); 568 (M^+), 549, 523, 427, 149, 122, 105, 77, 51, **10**: 2.1–2.9 (m, 2 H), 4.50 (t, 2 H), 5.7–6.5 (m); 518 (M^+), 499, 456, 427, 381, 357, 231, 219, 169, 131, 99, 77, 69, 55 (100). **11**[18]: 1.97 (m, 3 H), 2.05–2.85 (m, 2 H), 4.45 (t, 2 H), 5.67 (m, 1 H), 6.20 (m, 1 H); 532 (M^+), 513, 467, 427, 419, 293, 253, 211, 185, 113, 86, 69, 57, 43, 41, 39. **12**: 2.1–3.0 (m, 4 H), 3.1–3.3 (m, 2 H), 4.65 (t, 2 H); 396 (M^+), 283, 269, 249, 155, 135, 115, 99, 77, 69 (HRMS found 395.9457, calcd for $C_8H_8F_7IO_2$ 395.9457). **13**: 2.2–3.1 (m, 4 H), 4.73 (t, 4 H); 361 (M^+ − 21), 269, 249, 191, 155, 127, 99, 77, 69. **14**: 2.1–3.0 (m, 2 H), 3.90 (q, 2 H), 3.95 (t, 2 H); 545 (M^+ − 1), 507, 477, 427, 377, 357, 313, 181, 169, 149, 131, 113, 95, 77, 61, 51; 546 (CI, M^+). **15**: 3.7–4.1 (m, 4 H), 3.0–4.05 (m, 1 H); 672 (M^+), 573, 545, 427, 175, 131, 113 (100), 83, 69, 51. **16**: 1.25 (d, 3 H), 3.5 (m, 1 H); 574 (M^+), 427, 377, 169, 155, 141, 131, 119, 100, 77, 69 (two distinctive peaks are observed by GC/MS with 574 mass unit for the molecular ion. The pattern is very similar to that of $C_8F_{17}CH_2CH_2I$). **17**: 546, 353, 337, 313, 253, 211, 155, 113 (small) (two distinctive peaks are observed by GC/MS; we assume this is the isomer of **14**). **18**[18]: 2.1–3.0 (m), 3.87 (q, 2 H), 4.85 (t, 2 H); 461, 441, 405, 395, 219, 169, 131, 113 (100), 95, 77, 69. Anal. for C, H, Cl gave satisfactory results. IR gave typical absorption bands for covalently bound perchlorates; 1010, 1105, 1150, and 1215 cm^{-1}, as well as broad absorption band 3520 cm^{-1} for the OH stretching frequency). **19**: 1.93 (s, 3 H), 2.4–2.9 (m, 2 H), 3.41 (t, 2 H), 4.40 (q, 2 H); 587 (M^+), 568, 488, 462, 218, 168, 154, 113, 77, 56, 41 (HRMS found 587.0490, calcd for $C_{14}H_9NF_{20}O$ 587.0365).

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[24] Becker, J. Y.; Yatziv, S.; Zinger, B. *J. Org. Chem.* **1987**, *52*, 2783.