calcd for $C_{10}H_{15}N$ 149.1203, obsd 149.1199.

25c: IR 1670, 2250 cm^{-1}; NMR ($CDCl_3$) δ 1.62 (s, 3 H), 1.0–2.2 (m, 9 H), 2.24–2.46 (m, 2 H), 5.16–5.34 (m, 1 H). Anal. Calcd for $C_{10}H_{15}N$: C, 80.48; H, 10.13; N, 9.39. Found: C, 80.18; H, 10.21; N, 9.38.

25d: IR 1715 cm^{-1}; NMR ($CDCl_3$) δ 1.60 (s, 3 H), 1.04–2.26 (m, 9 H), 2.06 (s, 3 H), 2.36 (t, *J* = 7 Hz, 2 H), 5.12–5.28 (m, 1 H). (2,4-Dinitrophenyl)hydrazone: mp 73–75 °C. Anal. Calcd for $C_{17}H_{22}N_4O_4$: C, 58.95; H, 6.40; N, 16.19. Found: C, 58.85; H, 6.21; N, 16.06.

25e: IR 1670, 1740 cm^{-1}; NMR ($CDCl_3$) δ 1.56 (s, 3 H), 1.64 (s, 3 H), 0.92–2.16 (m, 13 H), 2.26 (t, *J* = 7 Hz, 2 H), 3.53 (s, 3 H), 4.84–5.06 (m, 1 H), 5.16–5.30 (m, 1 H). Anal. Calcd for $C_{16}H_{26}O_2$: C, 76.75; H, 10.43.

25f: IR 1050 cm^{-1}; NMR ($CDCl_3$) δ 1.58 (s, 3 H), 1.64 (s, 3 H), 1.4–2.3 (m, 13 H), 2.8 (t, *J* = 8 Hz, 2 H), 5.0–5.2 (m, 1 H), 5.2–5.4 (m, 1 H), 7.4–7.8 (m, 5 H); MS, *m/e* (M^+) calcd for $C_{20}H_{28}SO$ 316.1859, obsd 316.1873.

Registry No. **1** (R^1 = Me, R^2 = *n*-C_6H_{13}), 4609-91-0; **1** (R^1R^2 = $(CH_2)_4$), 2562-38-1; **1** (R^1 = $PhCH_2$, R^2 = Me), 17322-34-8; **1** (R^1 = Me, R^2 = Me_2CHCH_2), 66553-37-5; **1** (R^1R^2 = $(CH_2)_5$), 1122-60-7; **1** (R^1 = R^2 = Me), 79-46-9; **1** (R^1 = $PhCH_2$, R^2 = H), 6125-24-2; **1** (R^1 = Et, R^2 = H), 108-03-2; **1** (R^1 = R^2 = H), 75-52-5; **1** (R^1 = Ph, R^2 = H), 622-42-4; **1** (R^1 = CH_2COOMe, R^2 = H), 2483-57-0; **2** (R^3 = R^4 = H, Y = COME), 78-94-4; **2** (R^3 = Ph, R^4 = H, Y = COPh), 94-41-7; **2** (R^3 = R^4 = H, Y = COOEt), 140-88-5; **2** (R^3 = Ph, R^4 = H, Y = COOMe), 103-26-4; **2** (R^3 = H, R^4 = Me, Y = COOMe), 80-62-6; **2** (R^3 = R^4 = H, Y = CN), 107-13-1; **2** (R^3 = Me, R^4 = H, Y = CN), 4786-20-3; **2** (R^3 = H, R^4 = Me, Y = CN), 126-98-7; **2** (R^3 = R^4 = H, Y = CHO), 107-02-8; **2** (R^3 = R^4 = H, Y = SO_2Ph), 5535-48-8; **2** (R^3 = Ph, R^4 = H, Y = SO_2Ph), 5418-11-1; **2** (R^3 = R^4 = H, Y = S(O)Ph), 20451-53-0; **2** (R^3 = Me, R^4 = H, Y = COOMe), 18707-60-3; **2** (R^3 = R^4 = H, Y = COOMe), 96-33-3; **2** (R^3 = R^4 = H, Y = NO_2), 3638-64-0; **3a**, 2562-42-7; **3b**, 97763-86-5; **3c**, 89706-88-7; **3d**, 97763-87-6; **3e**, 5498-73-7; **3f**, 75919-28-7; **3g**, 89706-86-5; **3h**, 97763-88-7; **3i**, 97763-89-8; **3j**, 91152-56-6; **3k**, 97763-90-1; **3l**, 82981-43-9; **3m**, 97763-91-2; **3n**, 58921-79-2; **3o**, 97763-92-3; **3p**, 91152-57-7; **3q**, 61174-01-4; **3r**, 83565-90-6; **4a**, 18216-72-3; **4b**, 18216-75-6; **4c**, 97763-93-4; **4d**, 97763-94-5; **4e**, 10094-36-7; **4f**, 97763-95-6; **4g**, 97763-96-7; **4h**, 97763-97-8; **4i**, 1123-04-2; **4j**, 97763-98-9; **4k**, 97763-99-0; **4l**, 80699-63-4; **4m**, 57919-02-5; **4n**, 52075-20-4; **4o**, 97764-00-6; **4p**, 97764-01-7; **4q**, 1918-88-3; **4r**, 83565-92-8; **5a**, 89861-56-3; **6a**, 2235-83-8; **6b**, 2046-17-5; **7a**, 78695-40-6; **7b**, 97764-24-4; **8a**, 62067-32-7; **8a** (semicarbazone), 62067-33-8; **8b**, 97764-25-5; **9a**, 89706-87-6; **9b**, 80460-05-5; **9c**, 97764-02-8; **9d**, 97764-03-9; **9e**, 6277-67-4; **10a**, 14983-20-1; **10b**, 1454-59-7; **10c**, 54089-83-7; **10d**, 97764-04-0; **11a**, 97764-05-1; **11b**, 97764-06-2; **11c**, 97764-07-3; **11d**, 97764-08-4; **11e**, 97764-09-5; **12a**, 55267-97-5; **12b**, 66050-54-2; **12c**, 97764-10-8; **12d**, 80376-43-8; **12e**, 97764-11-9; **13a**, 97764-12-0; **13b**, 97764-13-1; **13c**, 5732-70-7; **13d**, 20592-04-5; **13e**, 97764-14-2; **14**, 81769-17-7; **15**, 90112-90-6; **16**, 97764-27-7; **17a**, 97764-29-9; **17b**, 83565-97-3; **18a**, 97764-28-8; **18b**, 83566-00-1; **19**, 97764-30-2; **20**, 97764-31-3; **21**, 70391-76-3; **22**, 34969-96-5; **23**, 83566-01-2; **24a**, 97764-15-3; **24b**, 97764-16-4; **24c**, 97764-17-5; **24d**, 97764-18-6; **24e**, 97764-19-7; **24f**, 97764-33-5; **25a**, 90611-59-9; **25b**, 97764-20-0; **25c**, 97764-21-1; **25d**, 97764-22-2; **25d** (dinitrophenylhydrazone), 97764-34-6; **25e**, 97764-23-3; **25f**, 97764-32-4; TMG, 113-00-8; DBU, 31171-04-7; $MeCHNO_2(CH_2)_2COOMe$, 10312-37-5; $MeCO(CH_2)_2CHNO_2(CH_2)_2COOMe$, 61426-51-5; CH=CHCH=CHMe, 504-60-9; 2-(phenylthio)-2-cyclopentenone, 34780-08-0; 2-(phenylsulfonyl)-2-cyclopentenone, 97764-26-6; 1-(nitromethyl)cyclopentene, 2562-42-7; 1-(nitromethyl)cyclohexene, 5330-61-0; 1-(nitromethyl)cycloheptene, 52315-51-2; isoprene, 78-79-5; myrcene, 123-35-3.

Stable Long-Chain Fluoroxy Compounds and Their Chemistry[†]

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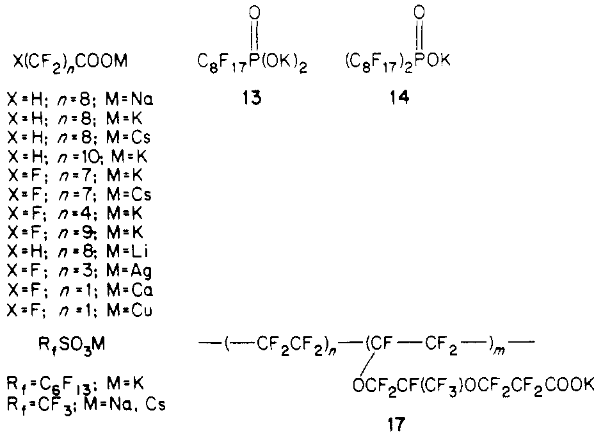
Certain alkalai metal salts of long-chain perfluorinated acids were reacted with nitrogen-diluted fluorine to produce oxidative solutions. The reaction conditions can be controlled to afford mainly acyl hypofluorites (R_fCOOF) or fluoroxy species [R_fCF_2OF and $R_fCF(OF)_2$] which have been identified by both chemical reactions and ^{19}F NMR studies. These solutions are useful in electrophilic fluorination reactions and as initiators for the polymerization of some fluorinated monomers. As initiators they produce polymers with fewer reactive end groups when compared with standard methods of initiation.

Introduction

The mild and selective introduction of fluorine into organic molecules continues to be of interest[1] because of potentially important applications to the areas of agrichemicals and pharmaceuticals.[2] A variety of electrophilic fluorinating agents including F_2,[3] CF_3OF,[4] CF_3CF_2OF,[5] XeF_2,[6] CF_3COOF,[7] and CH_3COOF[8] have been developed and utilized for this purpose. However, most of these materials are gaseous or highly volatile, some cannot be stored for long periods of time and ideally are prepared just prior to use, and some are too expensive for ordinary routine work. It was the objective of our program then to develop nonvolatile electrophilic fluorinating agents which could be conveniently handled and stored for long periods of time at least in solution. A possible answer to these problems seemed to lie in the preparation of the fluoroxy derivatives of long-chain perfluoroalkyl acids.

Chart I



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Discussion

A series of salts of long-chain perfluoro acids (Chart I) were suspended in fluorotrichloromethane (F-11), 1,1,2-trifluoro-1,2,2,-trichloroethane (F-113), or perfluoro-2-butyltetrahydrofuran (FC-75), cooled (−78 °C to −20 °C), and treated with fluorine diluted in nitrogen (1% to 10% partial pressure). Sodium salts [e.g., 1] reacted to form oxidative solutions, although slowly and in low yields, based on utilization of available fluorine. Potassium and cesium salts (**2**–**8**) also afforded oxidative solutions but in higher yields again based on fluorine. The lithium, silver, calcium, and copper salts (**9**–**12**) failed to react, however, and no oxidative materials were formed. Similarly, potassium salts of perfluoro phosphoric acids (**13** and **14**), perfluoro sulfonic acids (**15** and **16**), and of Nafion carboxylate (**17**) were prepared and treated with fluorine, but again no reaction was observed. Thus while reaction appears to be a function of both the cation and the anion, it is unclear at this time whether this is related to the solubility of the salt (which appears to be low in all cases) or from ion pairing between the two species.

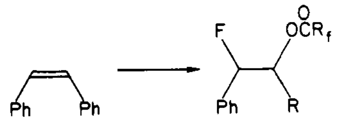
For a more detailed examination of these oxidative solutions for composition, stability, and use, we selected the potassium salt of the readily available *n*-perfluorooctanoic acid. Treatment of a suspension of anhydrous potassium perfluorooctanoate (**5**) in fluorotrichloromethane with fluorine (1% to 5% in nitrogen, partial pressure) results in the formation of an oxidative solution. Previous work[5,7] suggests that this oxidative power arises from the formation, depending upon reaction conditions, of three species, the fluoroxyperfluoroalkanes **18** and **19** and perfluorooctanoyl hypofluorite (**20**). The total concentration of the

$$\underset{\mathbf{5}}{CF_3(CF_2)_6COOK} \rightarrow$$

$$\underset{\mathbf{18}}{CF_3(CF_2)_7OF} + \underset{\mathbf{19}}{CF_3(CF_2)_6CF(OF)_2} + \underset{\mathbf{20}}{CF_3(CF_2)_6COOF}$$

oxidative materials was determined by titration with standard periodate after quenching with potassium iodide. The reaction mixtures after filtration of unreacted starting material and fluoride salts could then be stored as stable stock solutions in Pyrex vessels at −20 °C for months without appreciable loss of oxidative power.[9] After concentration the ^{19}F NMR of this reaction mixture was examined downfield of the $CFCl_3$ standard and indicated two signals in a ratio of 1:4. The stronger signal at +156.6 ppm was assigned to the bishypofluorite **19** and consisted of a quintet in the ratio of 1:2:2:2:1 with $^3J = 20$ Hz and $^4J = 10$ Hz. An additional splitting of $^5J = 1.5$ Hz was also observed due to further long-range coupling. The weaker signal at +146 ppm appeared as a singlet and was assigned to the acyl hypofluorite **20**. The relative ratio of **19**:**20** then was 2:1. It is also possible that the solution might contain other oxidative materials, such as hypofluorite **18**, but if in low concentrations and due to intensive splitting patterns, these would go undetected. The results were also identical whether the solutions were examined soon after preparation or after a day's storage at −20 °C.

Since it was reported[7] that the reaction of CF_3COONa with F_2 after addition of HF or H_2O to the reaction mixture favored the formation of trifluoroacetyl hypofluorite in preference to the other fluoroxy species, a similar study was undertaken with potassium perfluorooctanoate (**5**). The most consistent results were obtained by utilizing hydrated salt **5** ($CF_3(CF_2)_6COOK{\cdot}2H_2O$, 8% H_2O by Karl Fisher) prepared by recrystallization of the anhydrous material from water. Hydrated **5** was suspended in either F-11 or FC-75 and treated with nitrogen-diluted F_2. The filtered solutions were analyzed for perfluorooctanoyl hypofluorite by treating an aliquot with an excess of *cis*-stilbene (**21**), determining the yield of the adduct **22** by gas chromatography, and calculating the relative percentage of **20** to total oxidative species as determined by iodometric titration. ^1H and ^{19}F NMR (see Experimental Section) indicated chiefly syn addition of **20** affording the erythro isomer of **22** in >90% stereochemical purity.[7] For solutions prepared in this way, perfluorooctanoyl hypofluorite (**20**) typically represented 70–95% of the total oxidative power of the solution (as determined by iodometric titration). Similar analysis of solutions prepared from suspensions of anhydrous potassium perfluorooctanoate, however, afforded oxidative solutions which were typically only 20–40% in **20**.



21 **22**

$R_f = CF_3(CF_2)_6$

We next examined the usefulness of these solutions as sources of electrophilic fluorine and as polymerization initiators. Fluoroxy compounds such as **18** and **19** were expected to be excellent sources of electrophilic fluorine and indeed at low temperatures (−78 °C to −20 °C) with electron-rich olefins the oxidative solutions afforded products consistent with an electrophilic mechanism. Thus, with the whole oxidative mixture originating from the reaction of salts **1**–**8** with fluorine, functioning as a single homogeneous fluorinating agent, treatment of the enol acetates of tetralone (**23**), 3-oxo-5-androstan-17β-ol acetate (**24**), and methyl 3-oxo-glycyrrhetate (**25**) yielded the α-fluoro ketones α-fluorotetralone (**26**, 85%), 2α-fluoro-2-androstan-17β-ol acetate (**27**, 60%), and methyl 3-oxo-fluoroglyrrhetate (**28**, 85%) (see Scheme I). These yields were comparable with those obtained previously with CF_3COOF.[10]

In the presence of tetrafluoroethylene, homolytic fragmentation of the oxidative species occurred initiating homo- and copolymerizations. Polymerization began immediately upon mixing in either aqueous or fluorocarbon (FC-75, Freon −113) media down to at least 0 °C. With solutions high in acyl hypofluorite (70–95%) typical conversions to polymer were over 80% and long-lived polym-

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(1) (a) Schlosser, M. *Tetrahedron* **1978**, *34*, 3. (b) Gerstenberger, R. C.; Hass, A. *Angew. Chem., Int. Ed. Eng.* **1981**, *20*, 647.

(2) "Biomedical Aspects of Fluorine Chemistry", Filler, R., Kobayashi, Y., Ed.; Elsevier: New York; 1982.

(3) See, for example: (a) Alker, D.; Barton, D. H. R.; Hesse, R. H.; James, J. L.; Markwell, R. E.; Pechet, M. M.; Rozen, S.; Takeshita, T.; Toh, H. T. *Nouv. J. Chim.* **1980**, *4*, 239. (b) Rozen, S.; Gal, C.; Faust, Y. *J. Am. Chem. Soc.* **1980**, *102*, 6860. (c) Gal, C.; Rozen, S. *Tetrahedron Lett.* **1984**, *25*, 449. (d) Barton, D. H. R.; James, J. L.; Hesse, R. H.; Pechet, M. M.; Rozen, S. *J. Chem. Soc., Perkin Trans. 1* **1982**, 1105.

(4) Hesse, R. H. *Isr. J. Chem.* **1978**, *17*, 60.

(5) Lerman, O.; Rozen, S. *J. Org. Chem.* **1980**, *45*, 4122.

(6) Filler, R. *Isr. J. Chem.* **1978**, *17*, 71.

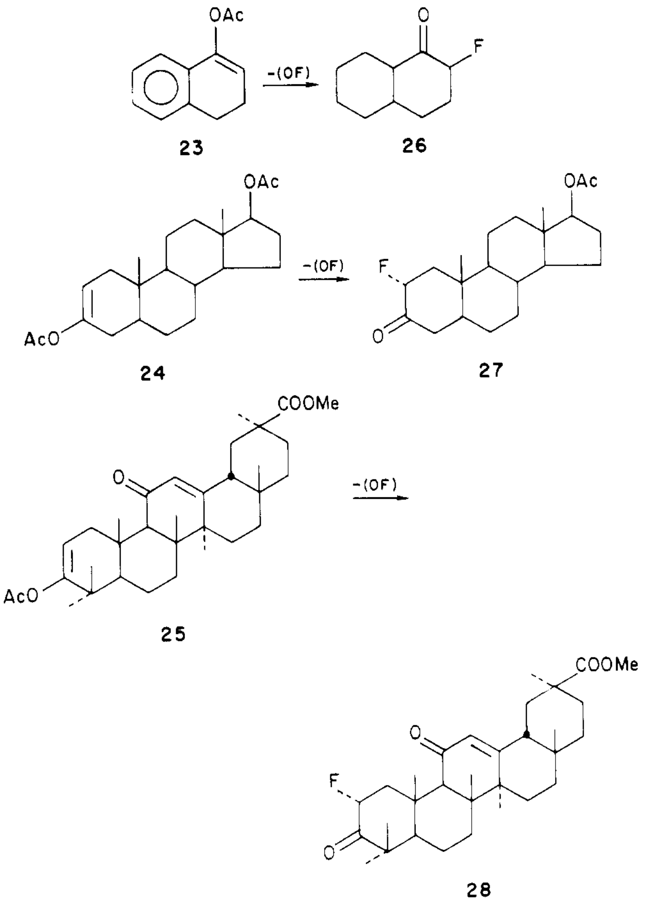
(7) Rozen, S.; Lerman, O. *J. Org. Chem.* **1980**, *45*, 672.

(8) Lerman, O.; Tor, Y.; Hebel, D.; Rozen, S. *J. Org. Chem.* **1984**, *49*, 806.

(9) Although highly concentrated solutions can be prepared (up to 80% v/v oxidizing solution in $CFCl_3$) by evaporating the solvent, such solutions should be handled with care and preferably at low temperatures since an unpredictable fast decomposition may occur at room temperature.

(10) Rozen, S.; Menahem, Y. *J. Fluorine Chem.* **1980**, *16*, 19.

Scheme I



erizations ($\geq$23 h) were observed. When, however, a solution consisting of only 20% to 40% of **20** was utilized, polymer yields fell below 20% to 40% and all polymerization activity frequently ceased within the first hour after mixing. The mechanism of the initiation remains unclear, but it appears that the acyl hypofluorite is the active initiator. The poor yields and rapid loss of polymerization with the other fluoroxy derivatives suggest that one or all of the other species (**18** and **19**) may actually be inhibitors of the process. With the acyl hypofluorite **20**, since polymerization starts immediately on mixing even at 0 °C, it is questionable whether the homolytic fragmentation occurs via discrete $R_fCOO\cdot$, $R_f\cdot$, and $F\cdot$ radicals or via an olefin–hypofluorite complex. In either case, the initiating fragment from the hypofluorite would remain attached to the polymer chain. Since virtually no carbonyl or other reactive end groups were detectable by IR in the polymer product, it is likely that any carboxy fragment $R_fCOO\cdot$ involved first loses CO_2 to produce R_f.

We are continuing to examine further the preparation, composition, and uses of these oxidative solutions.

Experimental Section

^{1}H NMR spectra were obtained with Varian EM 390 or IBM 80 spectrophotometers with tetramethylsilane as internal standard. ^{19}F NMR were obtained at 94.1 MHz on a Varian XL 100 spectrophotometer with fluorotrichloromethane as the internal standard. GC analyses were carried out on a HP 5840A gas chromatograph, using a Supelco 6 ft × 1/8 in. stainless steel column packed with 20% FS 1265 on 60/80 Gas Chrome R. The apparatus for the dilution and introduction of fluorine has been previously described.[5,7]

Preparation of Salts. General. Acid-salts were dissolved in water and titrated with an aqueous solution of the hydroxide with the desired counterion. Most of the solvent was then removed by passing a stream of nitrogen into the flask heated on a steam bath. Remaining water was removed in a vacuum oven (100 °C), thus affording anhydrous material.

Anhydrous Potassium Perfluorooctanoate. Potassium *tert*-butoxide (16.2 g, 144.9 mmol) was dissolved in anhydrous tetrahydrofuran (500 mL) under nitrogen. *n*-Perfluorooctanoic acid (60.0 g, 144.4 mmol) was dissolved in anhydrous tetrahydrofuran (500 mL), and the solution was added dropwise to the above mixture with stirring over 4 h. After stirring an additional hour, the solid was collected by vacuum filtration and washed with anhydrous tetrahydrofuran (500 mL) and anhydrous ether (500 mL). The solvent was removed by placing the material in a vacuum desiccator over phosphorus pentoxide for 24 h to yield the anhydrous potassium perfluorooctanoate as a white powder (56.36 g).

Potassium Perfluorooctanoate Hydrate. Anhydrous potassium perfluorooctanoate (30 g) was dissolved in water (200 mL) with heating. Crystallization was induced by cooling in ice (30 min). The solid was collected by vacuum filtration, and excess water was removed by suction (15 min) to yield the hydrate as white crystals (29.6 g), 8% water by Karl Fischer analysis.

Fluorination of Salts. General. The anhydrous or hydrated salts were suspended in solvent (F-11, F-113, or FC-75), and the mixture was cooled to −78 °C to −20 °C as desired. Fluorine diluted in nitrogen (5–10% partial pressure) was then passed into the mixture through a vibrating mixer shaft with the mixer adjusted for maximum dispersion of the gas. At various intervals, aliquots (10 mL) of the reaction mixture were taken and rapidly added to acidic (acetic acid) aqueous solutions of potassium iodide. The liberated iodine was then titrated with standard 0.01 M sodium thiosulfate. Upon reaching the desired concentration of oxidant, the cold mixture was filtered through glass wool and the solution stored at 0 °C to −20 °C. The following are typical examples of the procedure.

Fluorination of Potassium Perfluorooctanoate Hydrate. Freshly recrystallized potassium perfluorooctanoate hydrate (30 g) was suspended in FC-75 (450 mL) and the mixture cooled to −78 °C. Fluorine (5% in nitrogen, partial pressure, 66 mmol) was passed into the solution through a vibrating mixer shaft over 6 h. The cold reaction mixture was filtered through glass wool into an ice-cooled Pyrex erlenmeyer flask and the solution stored at −20 °C. Analysis by titration indicated a concentration of 25.2 mmol/L of oxidant after 33 mmol of fluorine had been added and 34.5 mmol/L after 66 mmol. This represents approximately a 24% utilization of available fluorine and a 26% conversion of the potassium perfluorooctanoate based on total oxidant produced.

For analysis of percent perfluorooctanoyl hypofluorite, a portion of the oxidizing solution (150 mL) was transferred to a reaction flask previously cooled to −10 °C and diluted with cold F-113 (150 mL). Titration before and after transfer and after dilution indicated no change in the quantity of oxidant. *cis*-Stilbene (3.83 g, 21.3 mmol) was then added in one portion in cold F-113 (20 mL) to the solution of the oxidants (5.3 mmol) and the mixture was stirred at −10 °C. After 10 min, retitration indicated the complete loss of oxidative power. The cold reaction mixture was washed with 10% sodium thiosulfate (200 mL) and 10% potassium bicarbonate (200 mL) and dried over magnesium sulfate. Filtration and removal of solvent under reduced pressure left an oil. GC analysis (200 °C, He 30 mL/min) of the oil after addition of 1-methoxynaphthalene as internal standard indicated that 81% of the total oxidant in solution (as determined by titration) was **20**.

Preparation of 1-Fluoro-2-(*n*-perfluorooctanoyl)-1,2-diphenylethane (22). An oxidizing solution was prepared as described in the previous example. A portion (150 mL) was transferred to a reaction flask previously cooled to −10 °C and diluted with cold F-113 (150 mL). Titration before and after transfer and after dilution remained unchanged. *cis*-Stilbene (1.35 g, 7.5 mmol) was added in one portion in cold F-113 (20 mL) to the solution of the oxidant (3.75 mmol), and the mixture was stirred at −10 °C. After 15 min, titration indicated that the solution had lost all oxidative power. The cold reaction mixture was washed with 10% sodium thiosulfate (200 mL), 10% potassium bicarbonate (200 mL), and saturated sodium chloride (200 mL) solutions and dried over anhydrous magnesium sulfate. Filtration, removal of solvent under reduced pressure, and purification by flash column chromatography (silica, hexane) yielded the adduct as a white crystalline solid (570 mg) >90% erythro (remaining, threo isomer).

Fluorination of Anhydrous Potassium Perfluorooctanoate. Anhydrous potassium perfluorooctanoate (7 g) was suspended in FC-75 (450 mL) and the mixture cooled to −78 °C under N_2. Fluorine (1% in nitrogen, partial pressure, 50 mmol) was passed into the solution through a vibrating mixer shaft over 12 h. The cold reaction mixture was filtered through glass wool into an ice-cold Pyrex erlenmeyer flask, and the solution was stored at −20 °C. Analysis by titration indicated a concentration of 2.95 mmol/L of oxidant after 10 mmol of fluorine have been added, 7.7 mmol/L after 20 mmol, 11.1 after 30, 14.25 after 40, 28.05 after 50, and 25.0 mmol/L after filtration. This represents approximately a 25% utilization of available fluorine and a 81% conversion of the acid salt based on total oxidant produced.

Analysis for perfluorooctanoyl hypofluorite was carried out as described previously on a portion of the solution (150 mL, 3.6 mmol of oxidant) and the percentage of **20** relative to total oxidant determined to be 28.5%.

Fluorination of Enol Acetates. A cold CH_2Cl_2 solution (−20 °C) of the enol acetates **23–25** (4.5 mmol) was added in one portion to 5 mmol of oxidizing solution originating either from the anhydrous or the hydrated potassium perfluorooctanoate. The mixture was well stirred for 1 to 2 min with the aid of the vibromixer, poured into thiosulfate solution, and washed with water until neutral. Flash chromatography and crystallization yielded the corresponding fluoro ketones **26–28** in 85%, 60%, and 85% yield, respectively, identical in all respects with the same fluoro ketones prepared with CF_3COOF.[10]

Initiation of Tetrafluoroethylene. A 500-mL polymer kettle was loaded with 200 mL of water and 1 g of perfluorooctanoic acid as surfactant. Oxygen was flushed from the system by pressuring to 90 psi with argon and evacuating to 100 mm, 3 times. A 1-L cylinder containing 33 g of tetrafluoroethylene was connected to the kettle and the system pressurized to atmospheric with tetrafluoroethylene. Then 15 mL of the initiator solution (4.5 mequiv/L) composed mainly of a perfluoroacyl hypofluorite as **20** was injected with stirring, and the kettle pressurized to 70 psi with tetrafluoroethylene. Once tetrafluoroethylene absorption ceased, the system was evacuated, and a second cylinder containing 33 g of tetrafluoroethylene was attached. After another 2 tetrafluoroethylene cylinders were emptied, the system was allowed to stand overnight. The following morning, a fifth tetrafluoroethylene cylinder was attached and it too was emptied below atmospheric pressure by the still living radical polymerization. The product was filtered, washed with 1:1 methanol–water, and dried to give 147 g (89%) of white poly(tetrafluoroethylene). The polymer was molded to a white plug at 372 °C. (The polymer, prepared similarly by using standard persulfate initiation, undergoes significant discoloration with gas evolution at this temperature.)

Initiation of Tetrafluoroethylene/Perfluoropropyl Vinyl Ether. A 500-mL polymer kettle was loaded with 200 mL of perfluoro-2-butyltetrahydrofuran and sealed. Three times the kettle was pressurized to 90 psi with argon; the contents of the kettle were stirred for 1 min, and then the pressure in the kettle was reduced to 100 mm, by evacuation to remove traces of oxygen. A 1-L cylinder containing 33 g of tetrafluoroethylene was attached to the kettle so as to permit introduction of tetrafluoroethylene as desired. Pressure in the kettle was brought to 14.7 psi by addition of tetrafluoroethylene from the cylinder. Next, 1 mL of perfluoropropylvinyl ether and then 5 mL of the hypofluorite solution **20** (as initiator) were injected into the kettle. When the tetrafluoroethylene cylinder was fully opened to the kettle, internal pressure was brought to 44 psi. After 92 min, pressure in the system had dropped to 10 psi. The resulting product was filtered, washed with CCl_2FCF_2Cl, and dried to give 31.13 g of solid white polymer. When extruded at 372 °C, the polymer gave a white, translucent product. (Again, copolymer prepared similarly by using standard persulfate initiation undergoes significant discoloration with gas evolution at this temperature.)

Long-Lived Trialkylamine Radical Cations Containing C_α–H Bonds in Acyclic Alkyl Groups

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Chemical reversibility is observed in the cyclic voltammogram of 9-neopentyl-9-azabicyclo[3.3.1]nonane (**3**), allowing measurement of its $E^{\circ\prime}$ value, 0.83 V vs. SCE in acetonitrile. Replacement of the *tert*-butyl group of **3** by isopropyl or phenyl leads to a much shorter radical cation lifetime, and $E^{\circ\prime}$ could not be reliably measured for the 9-isobutyl or 9-benzyl compounds **6** or **7**. The barrier for nitrogen inversion of **3**, which must be accompanied by NCH_2 rotation, is 12.0 kcal/mol at −10 °C, 5 kcal/mol higher than the barrier for its 9-ethyl analogue **9**. The dihedral angle between C_α–H and the nitrogen p orbital axis in the cation radical is argued to be important in determining cation radical lifetime. Observation of chemical reversiblity in the CV of 9-(2-adamantyl)-9-azabicyclo[3.3.1]nonane, **5**, required in situ drying of the solvent with alumina, as well as fast scan rates or low temperatures.

Trialkylamine radical cations are typically long-lived in strong acids but are very rapidly deprotonated at the α-carbon by the neutral amine.[1] This proton transfer is rapid enough that most trialkylamine cation radicals do not survive the milliseconds required to observe any cation reduction wave at 20 V/s scan rate in a cyclic voltammetry (CV) experiment[2] and give totally irreversible CV curves. The weakening of C_α–H bonds of amine cation radicals proves to be strongly dependent on the overlap with the half-filled p orbital at nitrogen, and the 9-azabicyclo-

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[1] Chow, Y. L.; Danen, W. C.; Nelsen, S. F.; Rosenblatt, D. H. *Chem. Rev.* **1978**, *78*, 243.

[2] Kochi and co-workers give a lifetime of 10^{-2}/(scan rate, V/s)s as the lifetime for first seeing a reduction wave in a CV curve (ref 6c, footnote 9), but this assumes perfect electrochemical reversibility and no distortion. It seems to us to be an overly optimistic lower limit in practice.

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