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1,1,2,2-Tetrafluoro-2-(polyfluoroalkoxy)ethanesulfonic Acids, 1,1,2,2-Tetrafluoro-2-(perfluoroalkoxy)ethanesulfonic Acids, and 2,2'-Oxybis(1,1,2,2-tetrafluoroethanesulfonic acid)

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Received November 3, 1987

Basic hydrolysis of 1,1,2,2-tetrafluoro-2-(polyfluoroalkoxy)ethanesulfonyl fluorides leads to new polyfluoroalkanesulfonic acids, $R_fOCF_2CF_2SO_3H$ ($R_f = CF_3CH_2$, $CF_3CF_2CH_2$, $CF_3CF_2CF_2CH_2$), after passing the aqueous solution through a strongly acidic resin. 1,1,2,2-Tetrafluoro-2-(perfluoroalkoxy)ethanesulfonic acids, $R_fOCF_2CF_2SO_3H$ ($R_f = CF_3CF_2$, $CF_3CF_2CF_2CF_2$) resulted when $I(CF_2)_nO(CF_2)_2SO_2F$ was fluorinated, subjected to basic hydrolysis, and distilled from H_2SO_4. Synthesis of the disulfonic acid $HSO_3CF_2CF_2OCF_2CF_2SO_3H$ was also accomplished.

Introduction

Tetrafluoroethane-β-sultone, $\overline{CF_2CF_2OSO_2}$, is a useful precursor to perfluoro and polyfluoro sulfonic acids. Earlier we reported the high-yield, straightforward preparation of polyfluoroalkyl esters of difluoro(fluorosulfonyl)acetic acid, viz.

$$\overline{CF_2CF_2OSO_2} + R_fOH \xrightarrow[-HF]{\text{base}} R_fOC(O)CF_2SO_2F^1$$

Fluorination of the carbonyl functionality with sulfur tetrafluoride in anhydrous hydrogen fluoride led to the corresponding α,α-difluoro ethers. This provides a general and direct synthetic route to tetrafluoro(polyfluoroalkoxy)ethanesulfonyl fluorides, $R_fOCF_2CF_2SO_2F$

$$R_fOC(O)CF_2SO_2F \xrightarrow[\Delta]{SF_4/HF} R_fOCF_2CF_2SO_2F^2$$

where R_f is polyfluoroalkyl.

Others have used $\overline{CF_2CF_2OSO_2}$ to synthesize totally fluorinated precursors to mono- and disulfonic acids by utilizing a different route:

$$CF_3(CF_2)_{n-1}O(CF_2)_2SO_2F \xrightarrow{NaOH} CF_3(CF_2)_{n-1}O(CF_2)_2SO_3Na^4$$
$$\uparrow[F]$$
$$\overline{CF_2CF_2OSO_2} \xrightarrow[KF]{ICl,\ C_2F_4} I(CF_2)_nO(CF_2)_2SO_2F^3 \xrightarrow{NaOH}$$
$$I(CF_2)_nO(CF_2)_2SO_3Na^4 \xrightarrow{Na_2S_2O_4} NaO_2S(CF_2)_nO(CF_2)_2SO_3Na^5 \xrightarrow{Cl_2}$$
$$ClO_2S(CF_2)_nO(CF_2)_2SO_3Na \xrightarrow{NaOH} NaO_3S(CF_2)_nO(CF_2)_2SO_3Na^4$$

We have taken advantage of these methods to prepare new polyfluoro- and perfluoroalkane sulfonic acids.

Fluorinated sulfonic acids and their derivatives have had wide chemical application.[3,6,7] Here we describe the synthesis of several new perfluoro- and polyfluorosulfonic acids that may be useful as additives to fuel cell electrolyte systems, as surfactants, or in other tasks requiring thermally and hydrolytically stable strong acids.

Results and Discussion

When standard methods of synthesis rather than electrochemical fluorination techniques are utilized to prepare sulfonic acids and their precursors, the steps necessary are numerous and time-consuming, and the purification coupled with removal of water requires repeated distillation at reduced pressure and elevated temperature. Synthesis of polyfluoro sulfonic acid precursors by the fluorination of the appropriate esters with sulfur tetrafluoride under mild conditions demonstrates clearly the value of the anhydrous hydrogen fluoride solvent system. Hydrolysis of the resulting sulfonyl fluorides occurs smoothly by using aqueous sodium hydroxide at 25 °C to give the sodium sulfonate salt, which must be separated from the concomitant product NaF by extended extraction with anhydrous C_2H_5OH. The alcohol-insoluble $R_fOCF_2CF_2SO_3Na$ is taken up in water and passed through a strongly acidic resin—Amberlite IR-120:

$$R_fOCF_2CF_2SO_2F \xrightarrow{NaOH} R_fOCF_2CF_2SO_3Na \xrightarrow[resin]{acidic} R_fOCF_2CF_2SO_3H(aq)$$

$$R_f = CF_3CH_2,\ CF_3CF_2CH_2,\ CF_3CF_2CF_2CH_2$$

After the volume of the resulting solution was reduced, P_4O_{10} was added and the anhydrous acid was slowly distilled out under reduced pressure. The acids are distilled as very viscous water-white liquids but often turn brown slowly on standing in a sealed Pyrex glass tube. These acids are stable to at least 150 °C as the neat compounds or in aqueous solution.

For perfluoro sulfonic acids, the tetrafluoroethane-β-sultone was reacted with KF, C_2F_4, and ICl to form $I(CF_2)_nO(CF_2)SO_2F$,[3] which can be fluorinated to lead to monosulfonic acids. However, it is interesting to note that while SbF_5 was used successfully to convert $I(CF_2)_nO(CF_2)_2SO_2F$ to $CF_3(CF_2)_{n-1}O(CF_2)_2SO_2F$ in 90% yield[8] ($n = 4$), when $n = 2$ the β-carbon–oxygen bond was broken.[9] The more traditional Swarts reaction proved to be a satisfactory method in this case:

$$I(CF_2)_2O(CF_2)_2SO_2F \xrightarrow[Cl_2]{SbF_3,\ SbCl_5} CF_3CF_2O(CF_2)_2SO_2F$$

In the synthesis of the disulfonic acid, the most crucial step is the conversion of $I(CF_2)_2O(CF_2)_2SO_3Na$ to $NaO_2S(CF_2)_2O(CF_2)_2SO_3Na$. This was accomplished by using $Na_2S_2O_4$ to give a 90% yield.[5] Each of the perfluoro sulfonic acids was obtained in hydrated form after distillation at temperatures between 80 and 100 °C and pressures ≤0.5 Torr. At room temperature each is a water-white, extremely viscous liquid that is stable as the neat compound or in aqueous solution at >125 °C.

Not surprisingly, all of the sulfonic acids described are highly hygroscopic and, although they can be purified adequately by distillation to meet the rigors of standard elemental analysis, purification to meet electrochemical standards is difficult.

Experimental Section

Materials. $I(CF_2)_2O(CF_2)_2SO_2F$, $I(CF_2)_4O(CF_2)_2SO_2F$, $CF_3CF_2O(CF_2)_2SO_2F$, $CF_3CF_2CF_2CH_2OCF_2CF_2SO_2F$, $CF_3CF_2CH_2OCF_2CF_2SO_2F$, and $CF_3CH_2OCF_2CF_2SO_2F$ were prepared according to the literature.[2,3]

General Procedures. ^{19}F NMR spectra were obtained on a JEOL FX-90Q Fourier transform NMR spectrometer operating at 84.26 MHz. DMSO-d_6, D_2O, and ethyl acetate were used as solvents with $CFCl_3$ as external reference. Chemical shifts upfield from $CFCl_3$ were assigned

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negative values. ^{1}H NMR spectra were obtained at an operating frequency of 89.56 MHz. Elemental analyses were performed by Beller Mikroanalytisches Laboratorium, Göttingen, W. Germany.

General Procedure for Polyfluoro Sulfonic Acids. With $CF_3CH_2OCF_2CF_2SO_2OH$ as an example, the procedure follows. $CF_3CH_2OCF_2CF_2SO_2F$ (13 mmol) was condensed into a flask at −196 °C that contained an aqueous solution of NaOH (1.08 g, 27.09 mmol) in 5.5 mL of water. The mixture was warmed to 25 °C. After the mixture was stirred for 48 h, the water was removed under vacuum, leaving solid $CF_3CH_2OCF_2CF_2SO_2ONa$ and NaF, which were placed in a Soxhlet extractor and extracted with absolute C_2H_5OH. Pure $CF_3CH_2OCF_2CF_2SO_3Na$ remained after the C_2H_5OH was evaporated. An aqueous solution of this salt was passed through an Amberlite IR-120 ion-exchange resin (strongly acidic gel-type resin). The volume of the aqueous acid was reduced, P_4O_{10} was added, and the anhydrous $CF_3CH_2OCF_2CF_2SO_2OH$ was distilled (65% yield). Also prepared in this manner were $CF_3CF_2CH_2OCF_2CF_2SO_2OH$ (60%) and $CF_3CF_2CF_2CH_2OCF_2CF_2SO_2OH$ (50%).

$CF_3CH_2OCF_2CF_2SO_2OH$. ^{1}H NMR δ 10.44 (s, OH), 4.6 (q, CH_2). ^{19}F NMR: ϕ −73.26 (tr tr, CF_3), −84.21 (complex, OCF_2), −116.7 (tr, CF_2S), $J_{CF_3-CH_2}$ = 8.79 Hz, $J_{OCF_2-CF_2S}$ = 1.83 Hz, $J_{CF_3-OCF_2}$ = 2.81 Hz. MS (EI): m/e 199 ($M - SO_3H^+$), 83 (CF_3CH_2). Anal. Calcd for $C_4F_7H_3O_4S$: C, 17.14; H, 1.07; F, 47.5. Found: C, 17.05; H, 1.15; F, 47.1.

$CF_3CF_2^BCH_2^COCF_2^DCF_2^ESO_2OH$. ^{1}H NMR: δ 11.20 (s, OH), 4.73 (tr, CH_2). ^{19}F NMR: ϕ −83.16 (s, CF_3), −84.79 (complex, OCF_2), −116.9 (tr, CF_2S), −123.2 (tr tr, CF_2), J_{C-B} = 13.19 Hz, J_{D-E} = 1.34 Hz. MS (EI): m/e 281 ($CF_3CF_2CH_2OCF_2CF_2S^+$). Anal. Calcd for $C_5F_9H_3O_4S$: C, 18.18; H, 0.91; F, 51.82. Found: C, 18.54; H, 1.01; F, 50.9.

$CF_3^ACF_2^BCF_2^CCH_2^DOCF_2^ECF_2^FSO_3^G$. ^{1}H NMR: δ 10.25 (s, OH), 4.75 (tr, CH_2). ^{19}F NMR: ϕ −80.67 (tr, A), −84.67 (complex, E), −116.8 (tr, F), −120.0 (complex, B), −127.1 (tr, C), J_{C-D} = 13.7 Hz, J_{A-B} = 8.78 Hz, J_{E-F} = 1.34 Hz. MS (EI): m/e 360 ($M - HF^+$), 280 ($CF_2CF_2CF_2CH_2OCF_2CF_2^+$). Anal. Calcd for $C_6F_{11}H_3O_4S$: C, 18.95; H, 0.79; F, 55.0. Found: C, 18.93; H, 0.89; F, 54.6.

Preparation of $CF_3(CF_2)_3O(CF_2)_2SO_2F$. Antimony pentafluoride (8.7 g, 40 mmol) was added dropwise to $I(CF_2)_4OCF_2SO_2F$ (10.5 g, 20 mmol) at 0 °C with stirring that was continued for 1 h. About 7 mL of H_2O was added dropwise to the mixture at 0 °C. After filtration, an oil layer was separated and $CF_3(CF_2)_3O(CF_2)_2SO_2F$ (7.5 g, 18 mmol) was obtained by distillation (90% yield). ^{19}F NMR (no solvent): ϕ 43.03, −83.92, −84.27, −85.08, −114.9, −128.5.

Preparation of $CF_3(CF_2)_3O(CF_2)_2SO_3Na$. A mixture of $CF_3(CF_2)_3O(CF_2)_2SO_2F$ and an equivalent amount of aqueous NaOH in a small amount of ethanol was stirred vigorously at 110 °C for 2 h. The mixture was maintained slightly alkaline at all times. After a small amount of acetone was added, the mixture was evaporated to dryness to give a white solid that was then extracted with boiling ethyl acetate. After the solvent was removed, the residue was a white solid that was dried to a constant weight at 100 °C (~100% yield). ^{19}F NMR (ethyl acetate): ϕ −82.47, −83.17, −83.28, −119.4, −127.5.

Preparation of $CF_3(CF_2)_3O(CF_2)_2SO_3H\cdot 2H_2O$. Into a 10 mL round-bottomed flask was placed $CF_3(CF_2)_3O(CF_2)_2SO_3Na$ (4.2 g, 9.6 mmol). Then, concentrated H_2SO_4 (4 g) was dropped into the flask with stirring that was continued at 110 °C for 2 h to give a colorless liquid that was distilled twice under reduced pressure to give $CF_3(CF_2)_3O(CF_2)_2SO_3H\cdot 2H_2O$ (3.5 g, 7.7 mmol, 80% yield); bp 91 °C (0.27 Torr). ^{19}F NMR for $CF_3^ACF_2^BCF_2^CCF_2^DOCF_2^ECF_2^FSO_3H\cdot 2H_2O$ (DMSO-d_6): ϕ −80.91 (t, J_{A-C} = 8.6 Hz, A), −126.4 (m, B and C), −83.28 (m, D), −82.15 (t, J_{D-E} = 13.4 Hz, E), −118.3 (s, F). ^{1}H NMR (DMSO-d_6) δ 5.57 (s). Anal. Calcd for $C_6H_5F_{13}O_6S$: C, 15.94; H, 1.12; F, 54.63; S, 7.09. Found: C, 16.14; H, 1.19; F, 56.2; S, 7.29.

Preparation of $CF_3CF_2O(CF_2)_2SO_3Na$. The compound was prepared in a manner similar to that for $CF_3(CF_2)_3O(CF_2)_2SO_3Na$. ^{19}F NMR (ethyl acetate): ϕ −82.70, −86.47, −88.20, −118.3.

Preparation of $CF_3CF_2O(CF_2)_2SO_3H\cdot H_2O$. The compound was prepared in a manner similar to that for $CF_3(CF_2)_3O(CF_2)_2SO_3H$ (80% yield); bp 82 °C (0.5 Torr). ^{19}F NMR for $CF_3^ACF_2^BOCF_2^CCF_2^DSO_3H\cdot H_2O$ (DMSO-d_6): ϕ −86.52 (s, A), −88.32 (t, B J_{B-C} = 12.8 Hz, B), −82.50 (t, C), −118.4 (s, D). ^{1}H NMR (DMSO-d_6): δ 6.43. Anal. Calcd for $C_4H_3F_9O_5S$: C, 14.38; H, 0.91; F, 51.18; S, 9.60. Found: C, 14.36; H, 0.89; F, 49.7; S, 9.20.

Preparation of $NaO_2S(CF_2)_2O(CF_2)_2SO_3Na$. Into a 250-mL three-necked round-bottomed flask were placed $ICF_2CF_2O(CF_2)_2SO_3Na$ (25 g, 56 mmol), $Na_2S_2O_4$ (19.5 g, 112 mmol), $NaHCO_3$ (9.4 g, 112 mmol), 27 mL of H_2O, and 10 mL of CH_3CN. Under a stream of nitrogen the contents were stirred vigorously at 90 °C for 12 h. After the solvents were removed, the residue was extracted three times with 40 mL of boiling ethyl acetate. The combined filtrates were evaporated to give a white solid that was recrystallized from isopropyl alcohol to give $NaO_2S(CF_2)_2O(CF_2)_2SO_3Na$ (20.5 g, 50 mmol, 89% yield). ^{19}F NMR for $NaO_2SCF_2^ACF_2^BOCF_2^CCF_2^DSO_3Na$ (ethyl acetate): ϕ −133.2 (A), −83.9 (B), −83.4 (C), −119.7 (D).

Preparation of $ClO_2S(CF_2)_2O(CF_2)_2SO_3Na$. Into a 100-mL three-necked round-bottomed flask were placed $NaO_2S(CF_2)_2O(CF_2)_2SO_3Na$ (20.5 g, 50 mmol) and 30 mL of H_2O. Then Cl_2 gas was bubbled through the solution at 0 °C for 4 h. A white solid (14.0 g, 33 mmol) was obtained by filtration (66% yield). ^{19}F NMR for $ClO_2SCF_2^ACF_2^BOCF_2^CCF_2^DSO_3Na$ (ethyl acetate): ϕ −109.1 (A), −79.7 (B), −82.4 (C), −118.3 (D).

Preparation of $NaO_3SCF_2CF_2O(CF_2)_2SO_3Na$. The compound was prepared in a manner similar to that for $CF_3(CF_2)_3O(CF_2)_2SO_3Na$. ^{19}F NMR for $NaO_3SCF_2^ACF_2^BOCF_2^BCF_2^ASO_3Na$ (D_2O): ϕ −82.53, −118.2. Anal. Calcd for $C_4F_8Na_2O_7S_2$: C, 11.38. Found: C, 11.57 (H <0.2%).

Preparation of $HO_3S(CF_2)_2O(CF_2)_2SO_3H\cdot H_2O$. The compound was prepared in a manner similar to that for $CF_3(CF_2)_3O(CF_2)_2SO_3H\cdot H_2O$ (74% yield); bp 99 °C (0.22 Torr). ^{19}F NMR for $HO_3SCF_2^ACF_2^BOCF_2^BCF_2^ASO_3H\cdot H_2O$ (DMSO-d_6): ϕ −117.3 (A), −82.9 (B). ^{1}H NMR (DMSO-d_6): δ 12.0. Anal. Calcd for $C_4F_8H_4O_8S_2$: C, 12.13; H, 1.02; F, 38.38; S, 16.19. Found: C, 12.24; H, 1.00; F, 38.20; S, 16.05.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, to the NSF (Grants CHE-8404974 and 8703790), to the AFOSR (Grant 87-0067), and to GRI for support of this work.