Journal of Fluorine Chemistry, 50 (1990) 31–46

Received: February 16, 1990; accepted: June 13, 1990

SULFONATION OF [2,3-DICHLOROPROPYL]TRIFLUOROETHYLENE: SYNTHESIS OF A NEW FLUORINATED β-SULTONE AND DERIVATIVES

JAVID MOHTASHAM, GARY L. GARD

Department of Chemistry, Portland State University, Portland, OR 97207-0751 (U.S.A.)

ZHEN-YU YANG and DONALD J. BURTON

Department of Chemistry, University of Iowa, Iowa City, Iowa 52242 (U.S.A.)

SUMMARY

Two new olefins, $CH_2BrCHBrCH_2CF=CF_2$ and $CH_2ClCHClCH_2CF=CF_2$, have been prepared as precursors to fluoro β-sultones. The new fluorinated sultone, $CH_2ClCHClCH_2\overline{CFCF_2OS}O_2$, was obtained (from the sulfonation of $CH_2ClCHClCH_2CF=CF_2$), along with its rearranged isomer, $CH_2ClCHClCH_2CF(SO_2F)C(O)F$, and hydrolysis product, $CH_2ClCHClCH_2CF(SO_2F)C(O)OH$.

INTRODUCTION

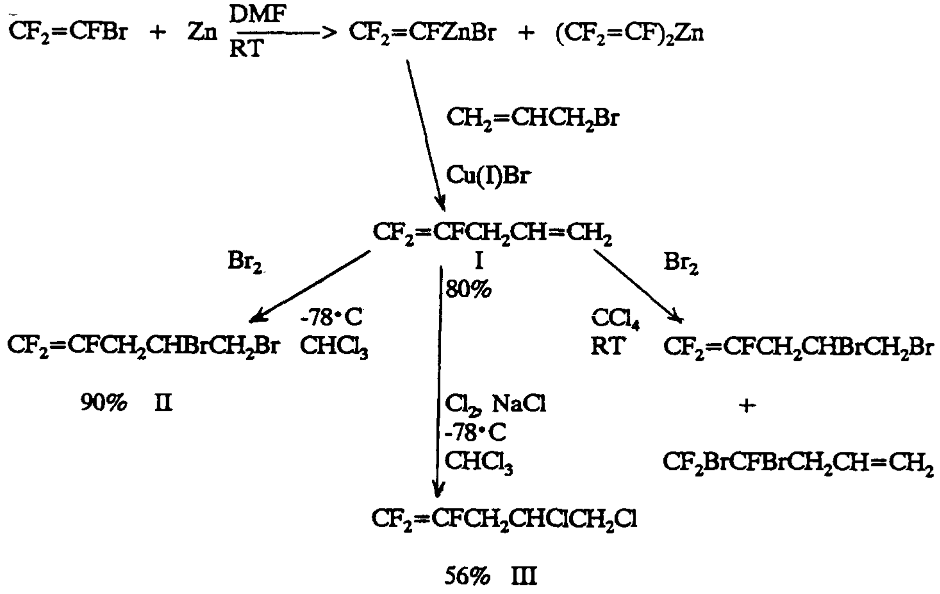
Fluorinated β-sultones are an important class of compounds which lead to derivatives containing the sulfonyl fluoride grouping (SO_2F). It is known that incorporating a sulfonyl fluoride group into a molecular system can produce compounds useful as ion-

0022-1139/90/$3.50

exchange resins, surface active agents and strong sulfonic acids [1-4]. Since fluorinated β-sultones lead to the new RSO_2F compounds, it is of considerable interest that new sultones with unique structural features be prepared. Although there are a number of fluorocarbon sultones, there are not fluoro β-sultones with hydrogen and halogens (Cl, Br, or I) in terminal positions. In order to prepare β-sultones of the type $XCH_2CHXCH_2\overline{CFCF_2OSO_2}$, the precursor olefins, $CH_2BrCHBrCH_2CF{=}CF_2$ (II) and $CH_2ClCHClCH_2CF{=}CF_2$ (III) were prepared using $CF_2{=}CFCH_2CH{=}CH_2$ (I). The sulfonation of the compound (III) resulted in the formation of the β-sultone, $CH_2ClCHClCH_2\overline{CFCF_2OSO_2}$ (IV), followed by a series of reactions that produced its rearranged isomer, $CH_2ClCHClCH_2CF(SO_2F)C(O)F$ (V), along with the hydrolysis product, $CH_2ClCHClCH_2CF(SO_2F)C(O)OH$ (VI).

RESULTS AND DISCUSSION

In order to prepare β-sultones of the type $XCH_2CHXCH_2\overline{CFCF_2OSO_2}$ (X=Cl, Br), it was necessary to prepare the following olefinic precursors $XCH_2CHXCH_2CF{=}CF_2$. In scheme I, a summary of the preparative routes used for the synthesis of $XCH_2CHXCH_2CF{=}CF_2$ is presented. It was found that bromination of $CF_2{=}CFCH_2CH{=}CH_2$ at room temperature gave a mixture of brominated products but at -78°C, bromination and chlorination gave the desired products in good yields; only the halogenation reactions at -78°C are reported.



Scheme I.

The reactions of monomer sulfur trioxide with $CH_2BrCHBrCH_2CF=CF_2$ (II) and $CH_2ClCHClCH_2CF=CF_2$ (III) were studied. The reactions were carried out in a modified Carius tube at 0•C. The result of these reactions was the formation of sultone from III.

$$\underset{III}{CH_2ClCHClCH_2CF=CF_2} + SO_3 \xrightarrow{0•C} \underset{IV}{CH_2ClCHClCH_2\overline{CFCF_2OS}O_2} \qquad (1)$$

In the case of $CH_2BrCHBrCH_2CF=CF_2$ (II) and monomer SO_3, nmr studies showed that the reaction resulted in the formation of a mixture which contains a β-sultone, $CH_2BrCHBrCH_2\overline{CFCF_2OS}O_2$, possibly $CH_2BrCHBrCH_2CFBrCF_2Br$, and unreacted olefin. We believe that SO_3 reacts with (II) forming Br_2 which then adds to the $-CF=CF_2$ bond. Since separation of the β-sultone was not possible, further study was discontinued.

Treatment of the β-sultone (IV) with metal halides, MX, (where M = Na or K, X = F or Br) produced the corresponding isomeric fluorosulfonyl acylfluoride:

$$IV + \xrightarrow[\Delta]{MX} CH_2ClCHClCH_2CF(SO_2F)C(O)F \qquad (2)$$

V

In the presence of water at 0°C, $CH_2ClCHClCH_2\overline{CFCF_2OSO_2}$ undergoes rearrangement, followed by hydrolysis:

$$IV + H_2O \longrightarrow CH_2ClCHClCH_2CF(SO_2F)C(O)OH + HF \qquad (3)$$

VI

The carboxylic acid (VI) is a stable compound which boils at 143±1°C/160 μ and melts at 54-58°C. It is interesting to note that with many fluorosultones, the acid product is unstable and undergoes decarboxylation at room temperature [3-8]:

$$X\overline{CFCF_2OSO_2} + H_2O \xrightarrow{-HF} [XCF(SO_2F)C(O)OH] \longrightarrow$$

$$XCF(SO_2F)H + CO_2 \qquad (4)$$

$X = SF_5, CF_3, CF_3O, CF_3O(CF_2)_2O, CF_2{=}CF(CF_2)_2, CF_2ClCFClCF_2$

It is believed that the instability of the intermediate carboxylic acids is due to formation of a stable $[XCF(SO_2F)]^-$ anion. However, when X = F, and H, a stable acid product is formed [1,9]. It is thought that the acid product is relatively stable when strong electron withdrawing and stabilizing groups adjacent to the CF group are absent. This results in the destabilization of the proposed intermediate anion, $[XCF(SO_2F)]^-$ and thereby favors stability of the parent acid.

The infrared spectra of all new compounds have several common features. The group frequencies and assignments in the infrared spectra of all compounds are: the OH absorption bands (near 3620 cm^{-1}); The $CF_2{=}CF$ and the $CH_2{=}CH$ olefinic vibrational bands (1799-1790 and 1644 cm^{-1}); the carbonyl stretching vibration (1871 and 1753 cm^{-1});

the SO_2 asymmetric and symmetric vibrational frequencies (1443-1413 cm^{-1} and 1224-1203 cm^{-1}); the carbon-fluorine absorption bands (1300-1100 cm^{-1}); the C-H vibrational bands (3089-2945 cm^{-1}); the intense S-F absorption band (near 800 cm^{-1}); and the carbon-chlorine absorption bands (near 590 cm^{-1}). In all cases these assignments are in excellent agreement with literature values [3,4,6-8].

The major mass spectral peaks for all compounds are listed in the experimental section. The molecular ions were observed for compounds I, II, and V. Additional $M-X^+$ peaks, such as $M-CF^+$, $M-Br^+$, $M-Cl^+$, $M-SO_2F^+$, were also found.

The ^{19}F nmr chemical shift values are summarized in Table I. For β-sultone, IV, the nonequivalent CF_2 fluorine resonances are found in the -82.3 to -86.8 ppm range; for other fluorinated sultones, $CF_2ClCFClCF_2\overline{CFCF_2OS}O_2$ and $CF_2{=}CF(CF_2)_2\overline{CFCF_2OS}O_2$, the CF_2 resonance bands are located in the -83.0 to -87.7 ppm range [4,7]. The resonance for the CF group with sultone IV in the four-membered ring is located at -145.3 ppm. This value is in good agreement with the literature values [3,6-8]. It is also found that consistent chemical shift values for similar groupings as $\underline{F}SO_2$, $\underline{CF}_2{=}$, and $=\underline{CF}$, are maintained for all compounds.

The ^{1}H nmr data for the new compounds are reported in Table II, and they are all self-consistent with respect to the expected chemical shifts. The coupling constants for the new compounds are reported in Table III and are also self-consistent with respect to the expected coupling constants.

The ^{13}C proton decoupled spectrum of the β-sultone, ${}^{a}CH_2Cl{}^{b}CHCl{}^{c}CH_2$-${}^{d}\overline{CF_{(1)}{}^{e}CF_{2(2)}OS}O_2$ shows five resonance groups between 32.4 to 118.9 ppm. These values for chemical shifts could be assigned to the β-sultone as follows: ${}^{a}C = 46.8$(s), ${}^{b}C = 51.7$(s), ${}^{c}C = 32.4$(d), ${}^{d}C = 118.9$(d,d,d), ${}^{e}C = 113.8$(d,d,d); the following coupling

TABLE I

FLUORINE NMR CHEMICAL SHIFTS[1,2,3]

	FSO_2	$CF_2{}^a$		$CF_2{}^b$		
		F_1	F_2	F_1	F_2	CF
I. $CH_2{=}CHCH_2CF{=}CF_2{}^b$	-	-	-	-105.9(d,d)	-124.8(d,d)	-174.0(d,d,t)
II. $CH_2BrCHBrCH_2CF{=}CF_2{}^b$	-	-	-	-102.4(d,d)	-121.7(d,d)	-175.8(d,m)
III. $CH_2ClCHClCH_2CF{=}CF_2{}^b$	-	-	-	-108.9(d,d)	-128.6(d,d)	-182.0(d,m)
IV. $CH_2ClCHClCH_2\overline{CFCF_2{}^aOS}O_2$	-	-82.3(d,d)	-86.8(d,d)	-	-	-145.3(d,m)
V. $CH_2ClCHClCH_2CF(SO_2F)C(O)F$	43.9(d,d)	-	-	-	-	-160.6(m)
VI. $CH_2ClCHClCH_2CF(SO_2F)C(O)OH$	43.0(d)	-	-	-	-	-159.3(d,m)

[1] Fluorine chemical shifts in ppm from external or internal (compounds I, II, III) $CFCl_3$.

[2] d = doublet, t = triplet, m = multiplet.

[3] The chemical shift for the $C(O)\underline{F}$ functional group in compound V was 32.1 ppm (d,m).

TABLE II

PROTON CHEMICAL SHIFTS[1,2,3]

	CH_2^a	CH_2^b	CH	C(O)OH
I. $CH_2{=}CHCH_2CF{=}CF_2$	5.19-5.22(m)	3.00(d)	5.93-5.64(m)	-
II. $CH_2BrCHBrCH_2CF{=}CF_2$	4.44-3.07(m)			
III. $CH_2ClCHClCH_2CF{=}CF_2$	3.83-3.03(m)	2.88-2.75(m)	4.36-4.13(m)	-
IV. $CH_2ClCHClCH_2\overline{CFCF_2OS}O_2$	4.2(m)	3.6(m)	4.8(m)	-
V. $CH_2ClCHClCH_2CF(SO_2F)C(O)F$	4.03(m)	3.4(m)	4.6(m)	-
VI. $CH_2ClCHClCH_2CF(SO_2F)C(O)OH$	4.4(m)	3.3(m)	5.25(m)	10.4(s)

[1] Proton chemical shifts in ppm downfield from external or internal (compounds I, II, III) TMS.

[2] d = doublet, m = multiplet.

[3] a = terminal $\underline{CH_2}$, b = $CH\underline{CH_2}$.

TABLE III

FLUORINE COUPLING CONSTANTS

	Coupling Constants (Hz)	
I. $CH_2=CHCH_{2(4)}CF_{(3)}=CF_{2(1,2)}$	$J_{1,2}=$ 88.0	$J_{2,3}=$ 115.0
	$J_{1,3}=$ 34.0	$J_{3,4}=$ 22.0
II. $CH_2BrCHBrCH_2CF_{(3)}=CF_{2(1,2)}$	$J_{1,2}=$ 80.6	$J_{2,3}=$ 115.0
	$J_{1,3}=$ 34.0	
III. $CH_2ClCHClCH_2CF_{(3)}=CF_{2(1,2)}$	$J_{1,2}=$ 80.5	$J_{2,3}=$ 114.0
	$J_{1,3}=$ 34.0	
IV. $CH_2ClCHClCH_2\overline{CF_{(3)}CF_{2(1,2)}OS}O_2$	$J_{1,2}=$ 107.2	$J_{2,3}=$ 7.1
	$J_{1,3}=$ 3.5	
V. $CH_2ClCHClCH_2CF_{(3)}(SO_2F)_{(2)}C(O)F_{(1)}$	$J_{1,2}=$ 6.1	
	$J_{2,3}=$ 2.3	
VI. $CH_2ClCHClCH_2CF_{(2)}(SO_2F)_{(1)}C(O)OH$	$J_{1,2}=$ 2.5	

constants were obtained, $J_{d,1}$ = 274.4 Hz and $J_{e,2}$ = 290.0 Hz. The coupling constant for $J_{e,2}$ is in good agreement with values reported for other sultone and cyclic systems; for $SF_5\overline{CHCF_2OS}O_2$, c-$C_4F_8$ and c-$C_4F_4Cl_4$ the corresponding J values are 293.0, 298.0 and 300.0 Hz, respectively [6,10]. We have also observed similar coupling constants for $J_{d,1}$ in other sultones, in $CF_3\overline{CFCF_2OS}O_2$ the coupling is 283.3 Hz [11].

EXPERIMENTAL

The SO_3 was obtained from Aldrich Chemical Company and distilled prior to use.

General Procedure. Gases were manipulated in a conventional Pyrex vacuum apparatus equipped with a Heise-Bourdon tube gauge and Televac thermocouple gauge. Infrared spectra were obtained by using a Pyrex-glass cell with KBr windows or as liquids between KBr disks on a Nicolet 20DX spectrometer. The nmr spectra were recorded with a Varian model EM-390 spectrometer operating at 90.0 MHz for proton and 84.67 MHz for the fluorine resonance and a General Electric model QE-300 spectrometer operating at 75.48 MHz for the carbon resonance. $Si(CH_3)_3$ and $CFCl_3$ were used either as external or internal standards. The mass spectra were taken on a VG-7070 HS mass spectrometer with an ionization potential of 70 eV. Perfluoro-kerosene was used as an internal standard.

Elemental analyses were determined by Beller Microanalytical Laboratory in Göttingen, Federal Republic of Germany.

Synthesis of $CF_2=CFCH_2CH=CH_2$

To a 1000 ml Pyrex-glass three-necked round-bottom flask, fitted with a Teflon magnetic stirring bar and a dry ice/isopropanol condenser which was connected to a source of nitrogen, were added 1000 mmol of acid-washed Zn powder and 500 ml of dry DMF. The $CF_2=CFBr$ was then added via the dry ice/isopropanol condenser with stirring at room temperature until the Zn powder disappeared. The reaction mixture was cooled to 0°C and 14 mmol Cu(I)Br was added; 830 mmol $CH_2=CHCH_2Br$ was slowly added via a syringe. When the addition was over, the mixture was stirred at room temperature overnight. The mixture was distilled (room temperature to 50°C) under vacuum to give DMF and $CF_2=CFCH_2CH=CH_2$. The DMF and $CF_2=CFCH_2CH=CH_2$ mixture was washed with water three times and dried over $MgSO_4$. Subsequent distillation gave 80 g of clear liquid $CF_2=CFCH_2CH=CH_2$, 655.7 mmol, in 80% yield; b.p. 38°C [12].

The infrared spectrum had the following bands (cm^{-1}): 3089 (w), 1796 (s), 1644 (m), 1291 (s), 1288 (s), 1264 (s), 1260 (s), 1254 (s), 1141-1132 (s), 1069 (s), 926 (s).

The ^{19}F nmr spectrum gave the following relative peak areas: CF_{2AB} (1.0, 1.0), and CF (1.0). The relative band areas for ^1H nmr were: CH_2 (2.0), CH_2 (2.0), and CH (1.0).

The positive ion mass spectrum (m/e) species: 122, M^+; 91, $[M\text{-}CF]^+$; 90, $[M\text{-}CFH]^+$; 84, $[M\text{-}2F]^+$; 71, $[M\text{-}CF_2H]^+$; 70, $[M\text{-}CF_2H_2]^+$; 66, $[MH\text{-}3F]^+$; 65, $[M\text{-}3F]^+$; 64, $[M\text{-}HF_3]^+$; 61, $[M\text{-}H_4F_3]^+$; 59, $[MH\text{-}C_2H_2F_2]^+$; 57, $CFCH_2C^+$; 50, CF_2^+; 45, $CFCH_2^+$, 44, $CFCH^+$; 41, $CH_2CH=CH_2^+$; 39, $C_3H_3^+$; 38, $C_3H_2^+$; 27, $C_2H_3^+$.

Synthesis of $CF_2=CFCH_2CHBrCH_2Br$

To a 1000 ml Pyrex-glass three-necked round-bottom flask, fitted with a Teflon magnetic stir bar and a pressure-equalized addition funnel, were added 295 mmol of $CF_2=CFCH_2CH=CH_2$ and 300 ml of $CHCl_3$. The mixture was cooled to -78°C and then a solution of 300 mmol Br_2 in 200 ml of $CHCl_3$ was slowly added via the addition funnel over 7 h. After the addition was completed, the mixture was warmed to room temperature and stirred overnight. The $CHCl_3$ was removed via rotary evaporation and the resulting residue was distilled to give 75 g of a colorless liquid, $CF_2=CFCH_2CHBrCH_2Br$, 266 mmol, in 90% yield; b.p. 27°C/2 mm.

The infrared spectrum had the following bands (cm^{-1}): 2983 (w), 1799 (s), 1796 (s), 1303 (s), 1298 (s), 1296 (s), 1274 (s), 1264 (s), 1243 (s), 1240 (s), 1238 (s), 1176 (s), 1094 (s).

The ^{19}F nmr spectrum gave the following relative peak areas: CF_{2AB} (1.0, 1.0) and CF (1.0). The relative band areas for ^1H nmr were: CH_2 (1.0), CH_2Br (2.0), and CHBr (1.0).

The positive ion mass spectrum (m/e) species: 284, M^+ [^{81}Br]; 282, M^+ [^{79}Br, ^{81}Br]; 280, M^+ [^{79}Br]; 203, $[M-^{81}Br]^+$; 201 $[M-^{79}Br]^+$; 187, $C^{81}BrCH^{81}Br^+$; 183, $C^{79}BrCH^{79}Br$, $[M-^{81}BrHF]^+$; 181, $[M-^{79}BrHF]$; 139, $CFCH_2CH^{81}Br^+$; 137, $CFCH_2CH^{79}Br^+$; 121, $CF_2{=}CFC_3H_4^+$; 108, $CH_2CH^{81}Br^+$; 107, $CH_2C^{81}Br^+$; 101, $C_5F_2H_3^+$; 95, $CF_2{=}CFCH_2^+$; 75, $CF_2{=}CCH^+$; 69, $CFCH_2CC^+$; 51, CCH_2CHC^+; 39, CH_2CHC^+.

Synthesis of $CF_2{=}CFCH_2CHClCH_2Cl$

To a 1000 ml Pyrex-glass three-necked round-bottom flask fitted with a Teflon magnetic stir bar and a pressure-equalized addition funnel, were added 330 mmol of $CF_2{=}CFCH_2CH{=}CH_2$, 170 mmol of NaCl, and 400 ml of $CHCl_3$. The mixture was cooled to -78•C and then a solution of 330 mmol of Cl_2 in 300 ml of $CHCl_3$ was slowly added via the addition funnel over 6 h. After the addition was completed, the mixture was warmed to room temperature with stirring overnight. The $CHCl_3$ was removed via rotary evaporation; the resulting residue was washed with water, and dried over $MgSO_4$. Distillation of the mixture gave 31.6 g of a colorless liquid, $CF_2{=}CFCH_2CHClCH_2Cl$, 184 mmol, in 56% yield, b.p. 65-68•C/10 mm.

The infrared spectrum had the following bands (cm^{-1}): 2945 (w), 1790 (s), 1420 (m), 1290 (s), 1240 (s), 1200 (s), 1100 (s), 1080 (s).

The ^{19}F nmr spectrum gave the following relative peak areas: CF_{2AB} (1.0, 1.0) and CF (1.0). The relative bands for ^1H nmr were: CH_2 (2.0), CH_2Cl (2.0) and CHCl (1.0).

Synthesis of $CH_2ClCHClCH_2\overline{CFCF_2OSO_2}$

To 26.2 mmol of $CH_2ClCHClCH_2CF=CF_2$ at 0°C in a 130 mL Pyrex-glass Carius tube equipped with a Kontes Teflon valve, 30.0 mmol of monomer SO_3 was added. Distillation of the mixture gave 3.17 g of clear liquid, $CH_2ClCHClCH_2\overline{CFCF_2OSO_2}$, 11.6 mmol, in 44.3% yield, b.p. 72-73°C/4 μ.

The infrared spectrum had the following bands (cm^{-1}): 3044 (vw), 2973 (w), 1482 (w), 1413 (vs, shoulder at 1447), 1375 (w), 1337 (m), 1314 (m), 1292 (m), 1268 (m), 1203 (vs, shoulder at 1243), 1122 (ms), 1059 (s), 1003 (wm), 968 (wm), 943 (w), 914 (vw), 869 (vw), 782 (s), 753 (m), 730 (w), 719 (w), 699 (vw), 679 (m), 656 (s), 638 (ms), 607 (sh), 580 (ms), 531 (ms), 520 (ms), 504 (sh), 484 (vw), 450 (vw), 424 (vw), 412 (w), 406 (sh).

The ^{19}F nmr spectrum gave the following relative peak areas: CF_{2AB} (1.0,1.0), and CF (1.0). The relative band areas for ^1H nmr were: CH_2 (2.1), CH_2Cl (2.2), and CHCl (1.0).

The positive ion mass spectrum (m/e) species: 239, $[M-{}^{37}Cl]^+$; 237, $[M-{}^{35}Cl]^+$; 173, $C^{37}ClC^{37}ClCCFS^+$; 171, $C^{37}ClC^{35}ClCCFS^+$; 169, $C^{35}ClC^{35}ClCCFS$; 161, $[CF(SO_2)CF_2(O)]^+$; 142, $CF_2CSO_3^+$; 127, $CH_2CHCC(SO_2)C^+$; 117, CF_2CFCCC^+; 108, $CF_2CFC_2H_3^+$; 97, $CFCF_2O^+$; 95, $CFSO_2^+$; 93, CF_2CFC^+; 81, CF_2CF^+; 80, SO_3^+; 79, $CFSO^+$; 64, SO_2^+; 62, CCF_2^+.

Anal. Calcd. for $C_5H_5F_3Cl_2SO_3$: C, 21.98; H, 1.83; F, 20.88; Cl, 26.01; S, 11.72. Found: C, 22.07; H, 1:81; F, 20.50; Cl, 25.90; S, 11.46%.

Synthesis of $CH_2ClCHClCH_2CF(SO_2F)C(O)F$

To a 25 mL Pyrex-glass round bottom flask, equipped with a Teflon-coated stirring bar, were added 10.2 mmol of dry NaF, and 9.89 mmol of $CH_2ClCHClCH_2\overline{CFCF_2OS}O_2$. The reaction vessel was heated to 40-50°C for 7 days. Distillation of the mixture gave 1.53 g of a clear liquid, $CH_2ClCHClCH_2CF(SO_2F)C(O)F$, 5.60 mmol, in 56.6% yield, b.p. 55±1°C/4μ.

The infrared spectrum had the following bands (cm^{-1}): 2992 (w), 2964 (w), 1871 (vs, shoulder at 1855), 1482 (w), 1443 (vs), 1391 (w), 1332 (ms), 1302 (ms), 1276 (ms), 1224 (vs, shoulder at 1244), 1172 (s, shoulder at 1201 and 1152), 1123 (sh), 1080 (ms), 1054 (ms), 1015 (ms, shoulder at 1028), 966 (w), 946 (w), 917 (w), 868 (m, shoulder at 851), 805 (s), 747 (ms, shoulder at 770), 724 (wm), 691 (wm), 658 (w), 639 (w), 609 (s), 580 (s), 537 (m), 521 (w), 495 (w), 485 (w), 459 (m), 442 (w, shoulder at 459), 426 (vw), 410 (w).

The ^{19}F nmr spectrum gave the following relative peak areas: FSO_2 (1.0), C(O)F, and CF (1.0). The relative band areas for ^1H nmr spectrum were: CH_2 (2.0), CH_2Cl (2.0), and CHCl (1.0).

The positive ion mass spectrum (m/e) species: 239, $[M\text{-}^{37}Cl]^+$; 237, $[M\text{-}^{35}Cl]^+$; 173, $C^{37}ClC^{37}ClCCFS]^+$; 171, $C^{37}ClC^{35}ClCCFS^+$; 169, $C^{35}ClC^{35}ClCCFS^+$; 161, $CF(SO_2F)C(O)F^+$; 155, $[M\text{-}^{37}Cl, HSO_2F]^+$; 154, $[M\text{-}H^{37}Cl, HSO_2F]^+$; 153, $[M\text{-}^{35}Cl, HSO_2F]^+$; 152, $[M\text{-}H^{35}Cl, HSO_2F]^+$; 143, $CH_2CHCC(SO_2)C(O)^+$; 127, $CH_2CHCC(SO_2)C^+$; 118, $CH_2CHCHCFC(O)F^+$; 100, $CH_2CHCH_2CFC(O)^+$; 95, $CFSO_2^+$; 83, SO_2F^+; 79, $CFSO^+$; 64, SO_2^+; 51, SF^+.

Anal. Calcd. for $C_5H_5Cl_2F_3SO_3$: C, 21.98; H, 1.83; F, 20.88; Cl, 26.01; S, 11.72. Found: C, 22.28; H, 1.74; F, 20.90; Cl, 26.37; S, 11.42%.

Synthesis of $CH_2ClCHClCH_2CF(SO_2F)C(O)OH$

To a 40 ml Kel-F vessel equipped with a Teflon stirring bar was added 10 ml of distilled H_2O. The reaction vessel was kept at ice bath temperature and 18.3 mmol of $CH_2ClCHClCH_2\overline{CFCF_2OS}O_2$ was added over a period of 25 minutes. After the addition was completed, the mixture was extracted with anhydrous Et_2O. The Et_2O was removed by distillation and the resulted residue was dried over $MgSO_4$. Subsequent distillation gave 3.33 g of a colorless viscous liquid, $CH_2ClCHClCH_2CF(SO_2F)C(O)OH$, 12.3 mmol, in 67.3% yield, b.p. 143±1°C/160μ; m.p. 56±2°C.

The infrared spectrum had the following bands (cm^{-1}): 3620 (br, m) 2974 (vw), 1753 (s), 1430 (vs), 1371 (w), 1335 (w), 1277 (m), 1264 (m), 1219 (vs), 1180 (s), 1156 (s), 1100 (m), 1064 (wm), 1034 (wm), 962 (w), 940 (w), 920 (w), 865 (wm), 807 (s), 745 (wm), 724 (w), 691 (w), 666 (vw), 616 (ms, shoulder at 644), 583 (s), 549 (w), 494 (w), 464 (vw), 441 (w).

The ^{19}F nmr spectrum gave the following relative peak areas: FSO_2 (1.0) and CF (1.2). The relative band areas for ^1H nmr were: CH_2 (1.8), CH_2Cl (1.9), CHCl (1.0) and C(O)OH (1.0).

The positive ion mass spectrum (m/e) species: 201, $[MH-Cl_2]^+$; 185, $[M-HCl_2, CH_2]^+$; 140, $CF(SO_2)C(O)OH^+$; 139, $CF(SO_2)C(O)O^+$; 127, $CF(SF)C(O)OH^+$; 124, $CF(SO)C(O)OH^+$; 112, $[M-CF(SO_2F)COOH]^+$; 109, $CH_2CSO_2F^+$; 101, $CH_2{}^{37}ClCH^{37}Cl^+$; 99, $CH_2{}^{35}ClCH^{37}Cl^+$; 97, $CH_2{}^{35}ClCH^{35}Cl^+$; 95, CSO_2F^+; 83, SO_2F^+; 79, $CSOF^+$; 76, $CFC(O)OH^+$; 67, SOF^+; 64, $SO_2{}^+$; 63, CSF^+; 51, SF^+.

Anal. Calcd. for $C_5H_6F_2Cl_2SO_4$: C, 22.15; H, 2.23; F, 14.02; Cl, 26.16; S, 11.83. Found: C, 22.26; H, 2.32; F, 14.2; Cl, 26.03; S, 11.72%.

ACKNOWLEDGEMENT

JM and GLG express their appreciation to the U.S. Department of Energy, Grant No. DE-FG21-88MC25142 for support of the work at PSU. ZY and DJB express their appreciation to NSF and AFOSR for support of the work at UI. Dr. Gary Knerr of the University of Idaho obtained the mass spectra. Drs. David H. Peyton and Robin J. Terjeson obtained and analyzed the ^{13}C nmr of the β-sultone.

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