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Synthesis and characterization of 1,2-bis(chlorosulfonyl)tetrafluoroethane and 1,2-bis(fluorosulfonyl)tetrafluoroethane

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Abstract

The new compound $ClO_2SCF_2CF_2SO_2Cl$ (**1**) is prepared by oxidative cleavage of the S–S bonds in the cyclic polysulfides $\overline{CF_2CF_2S_{3,4}}$ with chlorine and hydrogen peroxide. Compound (**1**) is converted in high yield to the bis(fluorosulfonyl)tetrafluoroethane $FSO_2CF_2CF_2SO_2F$ (**2**) by reaction with KF. This work represents an attractive alternative to the previously reported preparation of (**2**) by electrochemical fluorination (ECF).

Keywords: Oxidative cleavage; Cyclic polysulfides; Electrochemical fluorination

1. Introduction

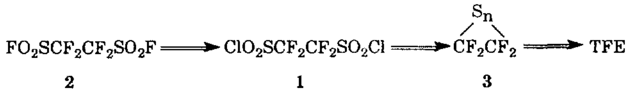
Perfluoroalkanesulfonyl fluorides R_fSO_2F can be obtained by electrochemical fluorination (ECF) of the corresponding alkanesulfonyl fluorides or chlorides [1–5]. An excellent alternative route for the synthesis of perfluoroalkanesulfonyl fluorides R_fSO_2F is the deiodosulfination of the corresponding perfluoroalkane iodide R_fI with Na_2SO_3 or $Na_2S_2O_4$. The resulting alkali sulfinates R_fSO_2M can be oxidized to the corresponding sulfonylchlorides R_fSO_2Cl. Further reaction with KF yields the alkanesulfonyl fluoride R_fSO_2F [6–9]. This alternative route works equally well for α,ω-diiodoperfluoroalkanes but fails in the case of diiodides $I(CF_2)_nI$ with $n<3$ [9,10]. 1,2-Diiodotetrafluoroethane reacts under elimination of iodine to form $CF_2{=}CF_2$.

As part of a program on fluorinated electrolytes for fuel cells and batteries [11], a sample of 1,2-bis(fluorosulfonyl)tetrafluoroethane $FO_2SCF_2CF_2SO_2F$ (**2**) was needed. This compound was previously obtained by ECF of $FO_2SCH_2CH_2SO_2F$ in modest yield [4]. While ECF is a well established method for preparing perfluorocarbon derivatives, it is not routine nor easily implemented. We sought a chemical synthesis of (**2**) from readily available starting materials. Herein the synthesis of (**2**) is described, starting with tetrafluoroethene (TFE) and sulfur.

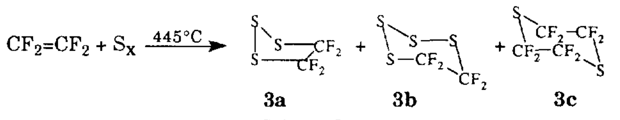
The retrosynthetic analysis for (**2**) focused on (**3**) which can be obtained from TFE and sulfur (Scheme 1) [12]. We believed that (**3**) could be converted to (**1**) under appropriate conditions and conversion of (**1**) to (**2**) would be straightforward. While the latter proved to be true, conversion of (**3**) to (**1**) proved much more demanding than expected.

The synthesis of (**3**) from TFE and sulfur proceeded well according to the published procedure as shown in Scheme 2 [12]. The main difficulty encountered was to keep the distilling sulfur sufficiently hot so that $S_x(g)$ was present to react with the TFE, otherwise conversion of TFE to products was low. On a representative run using 2.65 moles of TFE, the conversion of TFE to (**3**) was 61%, with 35% (**3a**), 61% (**3b**) and 4% (**3c**).

The conversion of (**3a,b**) to $ClSCF_2CF_2SCl$ is described in a patent using dry chlorine [13,14]. The conversion of $ClSCF_2CF_2SCl$ to $(ClO_2SCF_2CF_2S)_2$ by H_2O_2 was also



Scheme 1.



3a **3b** **3c**

Scheme 2.

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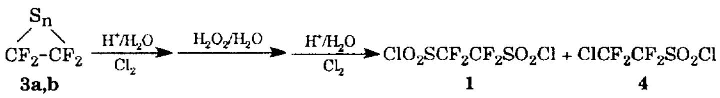
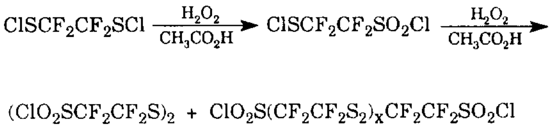


Scheme 3.



$$ClSCF_2CF_2SCl \xrightarrow[CH_3CO_2H]{H_2O_2} ClSCF_2CF_2SO_2Cl \xrightarrow[CH_3CO_2H]{H_2O_2}$$

$$(ClO_2SCF_2CF_2S)_2 + ClO_2S(CF_2CF_2S_2)_xCF_2CF_2SO_2Cl$$

Scheme 4.

reported [15]. Our initial plan was to use aqueous chlorine to convert (**3a,b**) to (**1**). However, under a variety of conditions this resulted in a complex mixture with incomplete oxidation of (**3a,b**) to (**1**). Ultimately we determined that a three-step, one-pot procedure could give excellent yields of (**1**) as shown in Scheme 3 with (**4**) being a minor byproduct.

Previous work on the oxidation of $ClSCF_2CF_2SCl$ with acidic H_2O_2 resulted in $(ClO_2SCF_2CF_2S)_2$ as shown in Scheme 4 [15]. It is likely that some of the species shown in Scheme 4 are present in our procedure. However, the complexity of the ^{19}F NMR (−80 to −95 ppm) cannot be explained by these products alone. At the end of the first chlorination, (**3a,b**) are no longer present but very little of (**1**) has been formed. Treatment with H_2O_2 results in a very exothermic reaction, increasing the amount of (**1**), with changes in the ^{19}F NMR (−80 to −95 ppm). Further chlorination then results in the disappearance of NMR signals (−80 to −95 ppm) and the further formation of (**1**) along with a minor amount of (**4**) as indicated in Scheme 3. The amount of (**4**) increases rapidly if the final chlorination is carried out above 22°C. We did not attempt to identify the intermediates in this reaction although both $ClSCF_2CF_2SCl$ and $ClSCF_2CF_2SO_2Cl$ can be seen in the ^{19}F NMR after the initial chlorination and some $ClSCF_2CF_2SO_2Cl$ is present after treatment with H_2O_2.

Conversion of (**1**) into (**2**) was readily accomplished in high yield using dry KF in sulfolane. Very dry conditions are needed to avoid the formation of hydrolyzed products $KO_3SCF_2CF_2SO_2F$ and $KO_3SCF_2CF_2SO_3K$. While sulfonyl fluorides are quite resistant to hydrolysis and the sulfonyl chloride is isolated from a water solution, KF in the presence of water greatly facilitates the hydrolysis of the sulfonyl halides to the sulfonate.

The new compound (**1**) and the previously known (**2**) were characterized by ^{19}F and ^{13}C NMR, IR and CI/MS as given in Section 2. The NMR of (**2**) is interesting in that all fluorines are coupled to the ^{13}C isotopomer in the ^{13}C spectra. In the ^{19}F spectra a deceptively simple A_4X_2-like pattern is observed.

In conclusion an effective but by no means simple method has been developed as an alternative to ECF for the preparation of $FO_2SCF_2CF_2SO_2F$. This compound is a useful synthon for a variety of new compounds, which are being actively investigated.

2. Experimental

2.1. General

^1H and ^{19}F NMR spectra were taken on a Bruker AC 200. (^1H/200.33 Mhz and ^{19}F/188.13 MHz) ^{13}C NMR spectra were taken on a Bruker AC 300 at 75.469 MHz. ^{19}F chemical shifts are referenced to internal $CFCl_3$ and ^{13}C to $CDCl_3$. IR spectra were recorded on a Perkin-Elmer 1600 series FTIR using a 10-cm gas cell fitted with KCl windows. Positive or negative ion chemical ionization mass spectra were obtained using a Fisons Trios 1000 GC-MS system operating at 70 eV. Samples were introduced by direct gas injection.

2.2. $ClSO_2CF_2CF_2SO_2Cl$ (1)

The cyclic polysulfides (**3a**) and (**3b**) [12] were dissolved in pentane, filtered and the pentane was removed by vacuum distillation. Chlorine gas was bubbled for four days into a suspension of 72.47 g (307.2 mmol) of the cyclic polysulfides (**3a,b**) in 20 ml H_2O, 20 ml CH_3COOH and 2 ml CF_3COOH. The initial temperature was maintained at 0°C for 1 day and then at 22°C. Chlorine was added until the ^{19}F NMR spectrum showed no signals for the starting material (**3a,b**). The reaction mixture was then cooled in an ice bath and 80 ml of 30% H_2O_2 were slowly added with an addition funnel. This produces a very exothermic reaction (Caution!) and gases were evolved after addition of the H_2O_2. After addition of the H_2O_2, the reaction mixture was slowly allowed to warm to 22°C over 1 h. At this time the ^{19}F NMR shows that only a ca. 25% of the mixture is the desired $ClSO_2CF_2CF_2SO_2Cl$ (**1**). Further attempts to increase the amount of (**1**) with H_2O_2 were unsuccessful. The aqueous layer was removed and 20 ml H_2O, 20 ml CH_3COOH and 2 ml CF_3COOH were added. After chlorination again for 2 days at 22°C, the ^{19}F NMR spectrum indicated the presence of $ClSO_2CF_2CF_2SO_2Cl$ along with a small amount of $ClCF_2CF_2SO_2F$ (**4**). The aqueous layer was then removed with a separatory funnel and the nonaqueous layer was washed twice with 10-ml portions of saturated NaCl–water. The liquid products (**1**) and (**4**) were separated by vacuum fractional condensation through traps at −50 and −196°C. The contents of the −50°C trap (**2**) were dried over P_4O_{10} and distilled under vacuum. The −196°C trap contained (**4**).

2.3. $ClO_2SCF_2CF_2SO_2Cl$ (2)

Yield 55 g, 59%; mp 24°C, bp 178°C (740 mm Hg); IR (5 Torr) 1477 (w), 1437 (vs), 1218 (s), 1200 (m), 1147 (s), 826 (w), 739 (m), 733 (s), 621 (m), 578 (m), 551 (s), 510 s) cm^{-1}; MS [Cl^-] CH_4, *m/z* 199/201 (10.7/4.1, M–SO_2Cl^-), 164 (10, $C_2F_4SO_2^-$), 99/101 (51,21, SO_2Cl^-), 83 (100, CF_2SH^- or SO_2F^-, ?), 85 (7, CF_3O^-, ?); NMR ($CDCl_3$) δ ^{19}F -103.5 (s); δ ^{13}C 114.6 (t–t); $^1J_{CF} = 312$, $^2J_{CF} = 34$ Hz.

2.4. *$ClCF_2CF_2SO_2F$* (**4**)

This compound was only identified by its NMR δ ^{19}F -66.9 (s, CF_2Cl), -105.3 (s, CF_2SO_2).

2.5. *$FO_2SCF_2CF_2SO_2F$* (**2**)

Potassium fluoride (30 g) which had been fused and ground to powder in a dry box was added to 20 ml of dry sulfolane in a one-piece 100-ml flask fitted with a glass–Teflon valve. Compound (**1**) (32 g) was then added by vacuum transfer to the flask at −196°C. The flask was placed in a −80°C bath and allowed to warm slowly to 22°C (ca. 2 h). The mixture was stirred for 2 days at 22°C and then the product (**2**) was collected under vacuum in a −75°C trap.

2.6. *$FO_2SCF_2CF_2SO_2F$* (**2**)

Yield 80%; mp -58 ± 2°C, bp 57°C (740 mm Hg); IR (10 Torr) 1475 (vs), 1283 (w), 1245 (vs), 1212 (vs), 1149 (vs), 1116 (w), 1062 (w), 1029 (w), 878 (m), 827 (vs), 805 (s), 784 (s), 778 (s), 615 (vs), 564 (vs) cm^{-1}; MS [CI] CH_4, *m/z* 267 (7, $M+1^+$), 183 (5, M–SO_2F^+), 133 (10, $CF_2SO_2F^+$), 119 (41, $C_2F_5^+$), 100 (8, $C_2F_4^+$), 69 (8, CF_3^+), 67 (100, SOF^+); NMR δ ^{19}F 47.7 (2F, quintet), -107.6 (4F, t), δ ^{13}C $FO_2S^{13}CF_2{}^{12}CF_2SO_2F$ (18 line multiplet, overlapping t–m), $^3J_{FF} = {}^4J_{FF} = 7.3$ $^1J_{CF} = 303$, $^2J_{CF} = 39$, $^2J_{CF} = 34$, $^3J_{CF} \simeq 1$ Hz.

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