December, 1973] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 3845—3848 (1973) 3845

The Electrochemical Fluorination of Dithiols and Cyclic Sulfides

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(Received April 26, 1973)

The electrochemical fluorination of dithiols [1,4-butanedithiol (I), 1,5-pentanedithiol (II), and 3-oxapentane-1,5-dithiol (III)] and cyclic sulfides [tetrahydrothiophene (IV), 2-methyltetrahydrothiophene (V), 3-methylthiophene (VI) and tetrahydrothiopyran (VII)] was conducted. Dithiols afforded the corresponding fully-fluorinated analogs of the starting dithiol ($SF_5(CF_2)_n SF_5$; $n=4$ from I, 5 from II; $SF_5CF_2CF_2OCF_2CF_2SF_5$ from III) and the cyclic products (perfluorotetramethylenesulfur tetrafluoride from I, perfluoro-2-methyltetramethylenesulfur tetrafluoride, perfluoro-3-methyltetramethylenesulfur tetrafluoride, and perfluoropentamethylenesulfur tetrafluoride from II, and perfluoro-4-oxapentamethylenesulfur tetrafluoride from III). The corresponding perfluoro-cyclic sulfur(VI) compounds were obtained from IV, V, VI, and VII in reasonable yields. The novel perfluoropolymethylene bis(sulfur pentafluoride)s are transparent heavy liquids. Their physical properties and ^{19}F NMR and IR data are reported.

So far little attention has been paid to the electrochemical fluorination of thiols,[1] though there have been intensive investigations of the electrochemical fluorination of sulfides.[2] However, it was shown recently that thiols were fluorinated electrochemically, and a number of partially-fluorinated alkyl-sulfur pentafluorides were found among the fluorination products.[3]

On the other hand, it has been known that perfluorocyclic sulfur(VI) compounds as well as the expected perfluoro-dialkylsulfur tetrafluorides were produced by the electrochemical fluorination of acyclic sulfur compounds containing one or more sulfur atoms in the alkyl chain.[2b,2c]

The present investigation was undertaken in order to elucidate the behavior of the electrochemical fluorination of such dithiols as 1,4-butanedithiol (I), 1,5-pentanedithiol (II), 3-oxapentane-1,5-dithiol (III), and also to investigate the possibility of their cyclization upon electrochemical fluorination and to compare the results with those of the fluorination of diols.[4] Further, the electrochemical fluorination of cyclic sulfides [tetrahydrothiophene (IV), 2-methyltetrahydrothiophene (V), 3-methylthiophene (VI) and tetrahydrothiopyran (VII)] was also examined.

Upon the electrochemical fluorination of dithiols, it was found that dithiols yielded a variety of products, as well as the corresponding novel perfluoropolymethylene bis(sulfur pentafluoride)s, as a result of fragmentation, degradation, and cyclization during the fluorination reaction.

On the other hand, the yields of the corresponding perfluorocyclic sulfur(VI) compounds upon the fluorination of cyclic sulfides were seriously affected by their ring size.

Results and Discussion

The reaction conditions and the results of the fluorination of dithiols and cyclic sulfides are summarized in Tables 1 and 2 respectively.

In anhydrous hydrogen fluoride, it is known[5] that thiols and sulfides dissolve to form a state of the sulfonium ion similar to that of compounds which contain an oxygen atom (oxonium ion). When these sulfonium compounds are subjected to oxidative fluorination by the electrochemical process, perfluoroalkyl derivatives of sulfur hexafluoride (R_f-SF_5 and R_f-SF_4-R_f'; $R_f = R_f' =$ perfluoro-alkyl group) are formed. At the same time, fluorocarbons and sulfur hexafluoride are also produced as major products as a result of the extensive cleavage of the C–S bond.

As may be seen in Table 1, the patterns of the fluorination products varied depending on the starting dithiols. It was also found that the composition of the products was drastically affected by the fluorination procedure. Thus, from I, perfluorotetramethylene bis(sulfur pentafluoride) was obtained in a yield of <1%, and from II, perfluoropentamethylene bis(sulfur pentafluoride) was obtained in a yield of 11.6%. However, perfluoro-3-oxapentamethylene bis(sulfur pentafluoride), $SF_5CF_2CF_2OCF_2CF_2SF_5$, could not be obtained from III (Run A) using the reaction procedure applied for the fluorination of I and II, but when III was fluorinated, while III was introduced into the electrolytic cell to maintain its concentration constant, a trace of the expected perfluoro-3-oxapentamethylene bis(sulfur pentafluoride) was obtained (Run B). These novel perfluoropolymethylene bis(sulfur pentafluoride)s are heavy, transparent, and odorless liquids. The physical properties and ^{19}F NMR and IR data of these compounds, together with those of perfluorotrimethylene bis(sulfur pentafluoride), which was prepared by the electrochemical fluorination of 1,3-propanedithiol (yield=2.5%), are shown in Tables 3, 4, and 5 respectively.

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TABLE 1. SUMMARY OF THE FLUORINATION OF DITHIOLS

Anodic current density, 3.3 A/dm^2; cell temp, 5—6 °C; sample, 0.20 mol

Sample	Volt	Electricity passed (A·hr)	Fluorinated compounds obtained (g)	Product (g)		
I	5.8—6.5	150	42.7	$SF_5CF_2CF_2CF_2CF_2SF_5$ (VIII) (0.6), n-$C_4F_9SF_5$ (IX) (12.2), $\overline{CF_2CF_2CF_2CF_2S}F_4$ (X) (2.9)		
II	7.2—7.7	177	52.2[a]	$SF_5CF_2CF_2CF_2CF_2CF_2SF_5$ (11.7), n-$C_5F_{11}SF_5$ (XI) (12.8), $\overline{CF(CF_3)CF_2CF_2CF_2S}F_4$ (XII) (0.6), $\overline{CF_2CF(CF_3)CF_2CF_2S}F_4$ (XIII) (0.2), $\overline{CF_2CF_2CF_2CF_2CF_2S}F_4$ (XIV) (0.3)		
III					A	B
Run A	5.5—6.6	152	57.6	$SF_5CF_2CF_2OCF_2CF_2SF_5$		(0.2)
Run B	5.5—5.6	151	40.3	$C_2F_5OC_2F_4SF_5$	(0.1)	(1.0)
				VIII	(0.2)	
				$SF_5CF_2CF_2SF_5$	(0.5)	(0.2)
				$(C_2F_5)_2SF_4$	(4.3)	(1.6)
				$\overline{CF_2CF_2OCF_2CF_2S}F_4$	(0.1)	(0.3)

a) 12.6 g of the product was obtained as cell drainings.

TABLE 2. SUMMARY OF THE FLUORINATION OF CYCLIC SULFIDES

Anodic current density, 3.3 A/dm^2; cell temp, 5—6 °C; sample, 0.20 mol

Sample	Volt	Electricity passed (A·hr)	Fluorinated compounds obtained (g)	Product (g)
IV	4.7—5.9	109	27.5	X (7.0), IX (9.1)
V	5.1—7.1	131	30.7	XII (0.9), XIII (0.4), XIV (0.2), XI (6.0), *iso*-$C_5F_{11}SF_5$ (1.3)
VI	5.7—6.8	109	27.8	XIII (3.3), XII (0.3), XIV (0.3), XI (0.7), *iso*-$C_5F_{11}SF_5$ (5.2)
VII	4.9—7.0	129	19.3	XIV (1.0), XIII (1.3), XII (0.5), XI (1.9), *iso*-$C_5F_{11}SF_5$ (0.5)

TABLE 3. PROPERTIES OF PERFLUOROPOLYMETHYLENE BIS(SULFUR PENTAFLUORIDE)S

Compound	Bp (°C)	n_D^{20}	d_4^{20}	Elemental analysis C	F
$SF_5CF_2CF_2SF_5$	84.0	1.2945	2.0397	6.49[a] (6.78)	75.4 (75.1)
$SF_5CF_2CF_2CF_2SF_5$	106.6	1.2988	2.0461	9.00 (8.91)	75.2 (75.2)
$SF_5CF_2CF_2CF_2CF_2SF_5$	127.4	1.3026	2.0521	10.57 (10.57)	74.7 (75.3)
$SF_5CF_2CF_2CF_2CF_2CF_2SF_5$	148.8	1.3059	2.0426	11.40 (11.91)	75.4 (75.4)
$SF_5CF_2CF_2OCF_2CF_2SF_5$	117.4	<1.28	1.9777	10.39 (10.21)	73.1 (72.8)

a) Calculated value in parenthesis.

TABLE 4. IR SPECTRA OF PERFLUOROPOLYMETHYLENE BIS(SULFUR PENTAFLUORIDE)S, cm^{-1}

$SF_5(CF_2)_2SF_5$: 1233 (s), 1163 (s), 903 (vs), 885 (ms, sh), 812 (w), 795 (w), 755 (s), 687 (w), 608 (ms), 578 (ms).

$SF_5(CF_2)_3SF_5$: 1244 (s), 1220 (ms), 1166 (s), 904 (vs), 892 (s), 865 (ms), 797 (w), 781 (w), 756 (w), 712 (s), 690 (ms), 611 (w), 594 (s), 573 (ms).

$SF_5(CF_2)_4SF_5$: 1241 (s), 1199 (w), 1169 (s), 902 (vs), 884 (s), 851 (w), 818 (w), 795 (w), 780 (ms), 754 (w), 737 (w), 711 (w), 691 (ms), 659 (w), 601 (ms), 567 (ms).

$SF_5(CF_2)_5SF_5$: 1261 (w, sh), 1240 (s), 1223 (ms, sh), 1169 (s), 1146 (w), 1036 (w), 941 (w), 901 (vs), 881 (ms), 873 (s), 838 (w), 806 (ms), 784 (w), 775 (w), 745 (ms), 704 (w), 692 (ms), 675 (w), 656 (ms), 608 (ms), 579 (ms), 558 (ms).

$SF_5CF_2CF_2OCF_2CF_2SF_5$: 1350 (w), 1310 (w), 1259 (ms), 1230 (s), 1206 (ms), 1191 (ms, sh), 1168 (s), 1133 (ms), 901 (vs), 858 (s), 818 (w), 797 (w), 778 (w), 758 (w), 726 (w), 703 (w), 690 (w), 678 (w), 643 (w), 611 (ms), 576 (w).

TABLE 5. ^{19}F NMR DATA OF PERFLUOROPOLYMETHYLENE BIS(SULFUR PENTAFLUORIDE)S AND PERFLUOROPENTAMETHYLENESULFUR TETRAFLUORIDE

Compound	Chemical shift, ppm				
	α CF_2[a]	β CF_2[a]	γ CF_2[a]	SF_{eq}[b]	SF_{ax}[b]
$SF_5CF_2CF_2SF_5$	18.3			−44.0	−61.8
$SF_5CF_2CF_2CF_2SF_5$	16.0	46.3		−44.3	−62.8
$SF_5CF_2CF_2CF_2CF_2SF_5$	17.3	44.5		−44.3	−62.8
$SF_5CF_2CF_2CF_2CF_2CF_2SF_5$	16.8	42.8	44.8	−44.3	−62.8
$SF_5CF_2CF_2OCF_2CF_2SF_5$	22.5	6.4		−44.2	−62.0
$\overline{CF_2CF_2CF_2CF_2CF_2SF_4}$	18.5	45.8	50.3	−19.8	−48.0

a) Chemical shift from external CF_3COOH. b) Chemical shift from internal CCl_3F.

TABLE 6. PROPERTIES OF PERFLUOROCYCLIC S(VI) COMPOUNDS, AND PERELUORO-*n*- AND ISOAMYLSULFUR PENTAFLUORIDES

Compound	Bp (°C)	n_D^{20}	d_4^{20}	Elemental analysis C	F
$\overline{CF_2CF_2CF_2CF_2CF_2SF_4}$[a]	95.2				74.0 (74.3)[b]
$\overline{CF_2CF(CF_3)CF_2CF_2SF_4}$	88.3	1.3017	1.9431	16.42 (16.76)	75.1 (74.3)
$\overline{CF(CF_3)CF_2CF_2CF_2SF_4}$	84.7	1.3056	1.9540	16.40 (16.76)	74.2 (74.3)
n-$C_5F_{11}SF_5$	92.5	1.2797	1.8885	15.33 (15.15)	77.1 (76.8)
iso-$C_5F_{11}SF_5$	92.5	1.2867	1.9252	15.06 (15.15)	76.5 (76.8)

a) Mp 19—21 °C, glassy. b) Calculated value in parenthesis.

By analogy with the results of the electrochemical fluorination of diols,[4] the cyclic products (perfluorotetramethylenesulfur tetrafluoride from I. perfluoropentamethylenesulfur tetrafluoride, perfluoro-2-methyltetramethylenesulfur tetrafluoride, and perfluoro-3-methyltetramethylenesulfur tetrafluoride from II. perfluoro-4-oxapentamethylenesulfur tetrafluoride from III) were also formed. Among them, the yield of perfluorotetramethylenesulfur tetrafluoride from I amounted to 4.7%.

As for the results with the fluorination of cyclic sulfides (Table 2), five-membered perfluorotetramethylenesulfur tetrafluoride from IV was obtained in the highest yield (11.4%). However, the results of the fluorination of V, VI, and VII indicated that considerable ring isomerization took place, resulting in a reduction of the yield of the expected sulfur(VI) compounds. The perfluorotetramethylenesulfur tetrafluoride[6] and perfluoropentamethylenesulfur tetrafluoride are solid at room temperature and freeze to a glass, while perfluoro-2-methyltetramethylenesulfur tetrafluoride and perfluoro-3-methyltetramethylenesulfur tetrafluoride are liquids. Although the five- and six-membered perfluorocyclic sulfur(VI) compounds were obtained in this manner, the four-membered perfluorotrimethylenesulfur tetrafluoride could not be obtained by the electrochemical fluorination of trimethylene sulfide, as it immediately polymerized in anhydrous

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hydrogen fluoride, thus giving an orange, gelatinous polymer.[7] The properties of these perfluorocyclic sulfur(VI) compounds, and those of perfluoro-*n*-amylsulfur pentafluoride and perfluoroisoamylsulfur pentafluoride are shown in Table 6. The structures of these perfluoroalkylsulfur(VI) compounds were determined by means of their ^{19}F NMR, mass, and IR spectra as well as by elemental analysis. However, the ^{19}F NMR spectra[8] of both perfluoro-2-methyltetramethylenesulfur tetrafluoride and perfluoro-3-methyltetramethylenesulfur tetrafluoride were too complicated to resolve because of the conformational rigidity of their molecules, which resulted in a non-equivalence of the geminal fluorines of the alkyl group, and also because they were a mixture of their respective geometric isomer.

Experimental

Reagents and Apparatus. All the reagents except 1,3-propanedithiol and 1,5-pentanedithiol were purchased from Tokyo Kasei Co., and were used as received. The 1,3-propanedithiol[9] and 1,5-pentanedithiol[10] were prepared by the reaction of the corresponding alkyl bromides with an alcoholic KSH solution, following the method of the reference. They were used after purification. The purity of the anhydrous hydrogen fluoride was higher than 99.5%.

All the features of the apparatus and the electrolytic cell (capacity, 1 l; electrode, Ni plates; effective anodic surface area, 9.2 dm²) used for this fluorination were the same as have been described previously.[4] A Shibata micro-pump, Model SPC-100, was used to change the 3-oxapentane-1,5-dithiol into the cell during the electrolysis.

The IR spectrum measurements were accomplished by means of a Hitachi EPI-G3 spectrometer, using a 6-cm gas cell with KBr windows.

The ^{19}F NMR spectra were obtained by a JEOL C-60-H high resolution spectrometer (56.4 Mc for ^{19}F), using trifluoroacetic acid (external) and trichlorofluoromethane (internal) for the determination of the chemical shifts.

Procedures. The general procedures for the fluorination of dithiols and cyclic sulfides were the same as have been described previously.[4] As examples, the fluorination of 1,5-pentanedithiol, 3-oxapentane-1,5-dithiol (Run B) and tetrahydrothiopyran will be described.

Fluorination of 1,5-Pentanedithiol: A 27.2 g portion of 1,5-pentanedithiol was introduced into a cell which contained 1 l anhydrous hydrogen fluoride. Then the electrolysis was carried out with an anodic current density of 3.3 A/dm², a cell voltage 7.2—7.7 V, and cell a temperature of 5—6 °C. He (50 ml/min) was introduced from the bottom of the cell in order to agitate the solution. The electrolysis was then conducted for 177 A·hr.

The evolving gases from the cell were passed through a reflux condenser kept at −25 °C, over NaF pellets, and then bubbled through an alkaline solution of sodium sulfite, containing a small amount of potassium iodide in a series of Ichinose gas washers, and finally collected through traps immersed in liquid nitrogen. After the electrolysis was over, the transparent heavy liquid, which was later found to consist mostly of perfluoropentamethylene bis(sulfur pentafluoride), was drained from the bottom of the cell, washed with an alkaline solution, dried over anhydrous sodium sulfate, and subsequently analysed by glc.

The fluorinated products (39.6 g) collected in the cold traps were carefully separated into two fractions using the traps of the low-temperature distillation unit : Fraction 1 (compounds having lower bp's); (20.4 g), Fraction 2; (19.2 g). The compounds in Fraction 1 consisted mainly of SF_6. Then, the volatile compounds in Fraction 2 were removed by distillation. Thus, 12.6 g of the distillation residue were obtained. The volatile distillate was identified as a mixture of perfluoro-*n*- and -*iso*-pentane (n-C_5F_{12} : iso-C_5F_{12}=90 : 10) by glc (column: Kel F # 3 30% on Chromosorb PAW, carrier; He) and on the basis of their known IR spectra. The cell drainings (17.4 g) and the distillation residue of Fraction 2 (12.6 g) were subsequently analysed by glc (column; Kel F # 90 26% on Chromosorb PAW, and DNP 25% on Shimalite, carrier; He). The following perfluorinated sulfur(VI) compounds were thus obtained: $SF_5(CF_2)_5SF_5$ 11.7 g, n-$C_5F_{11}SF_5$ 12.8 g, $\overline{CF(CF_3)CF_2CF_2CF_2SF_4}$ 0.6 g, $\overline{CF_2CF(CF_3)CF_2CF_2SF_4}$ 0.2 g, $\overline{CF_2CF_2CF_2CF_2CF_2SF_4}$ 0.3 g. These new compounds were characterized by means of their ^{19}F NMR, IR and mass data as well as elemental analyses (C and F).

Fluorination of 3-Oxapentane-1,5-dithiol (Run B): The fluorination was carried out in essentially the same manner illustrated above. However, the 3-oxapentane-1,5-dithiol was fed into the cell little by little by means of the micro-pump, which was connected with the sample injector,[2e] at a rate of about 5.5 ml/hr during electrolysis (anodic current density, 3.3 A/dm². cell voltage, 5.5—7.1 V. cell temp, 5—6 °C). For this sample feeding (27.6 g), 4 hr were required. Electrolysis was then continued for another hour. Thus, 151 A·hr of the electrolysis were conducted. No perfluorinated products were found in the cell drainings. The products (40.3 g), which was collected into traps immersed in liquid nitrogen, were similarly treated. The volatile $C_2F_5OC_2F_5$ and SF_6 were formed as major products. The following compounds were obtained by finally analysing the 4.7 g of the distillation residue: $SF_5CF_2CF_2OCF_2CF_2SF_5$ 0.2 g, $C_2F_5OC_2F_4SF_5$ 1.0 g, $SF_5CF_2CF_2SF_5$ 0.2 g,$(C_2F_5)_2SF_5$ 1.4 g, $\overline{CF_2CF_2OCF_2CF_2SF_4}$ 0.3 g.

Fluorination of Tetrahydrothiopyran: Tetrahydrothiopyran (20.4 g) was subjected to electrochemical fluorination under the following electrolysis conditions: anodic current density, 3.3 A/dm². electricity passed, 129 A·hr. cell voltage, 4.9—7.0 V. cell temp, 5—6 °C. The fluorinated product (19.3 g) was collected in traps cooled in liquid nitrogen. The product was initially subjected to a low-temperature distillation. The fraction (7.5 ml, 14.6 g) which has a bp of above 0 °C was treated likewise, and the following compounds were obtained. $\overline{CF_2CF_2CF_2CF_2CF_2SF_4}$ 1.0 g, $\overline{CF_2CF(CF_3)CF_2CF_2SF_4}$ 1.3 g, $\overline{CF(CF_3)CF_2CF_2CF_2SF_4}$ 0.5 g, n-$C_5F_{11}SF_5$ 1.9 g, iso-$C_5F_{11}SF_5$ 0.5 g. The ratio of the perfluoro-*n*- and -*iso*-pentane which was formed as a result of the cleavage of the C–S bond was as follows. n-C_5F_{12} : iso-C_5F_{12}=58 : 42.

The authors wish to thank Mr. Kazuo Kodaira for the mass measurements.

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7) See also R. W. Bost and M. W. Conn, *Ind. Eng. Chem.*, **25**, 526 (1933).

8) The chemical shifts of CF_3- at the 2- and 3- positions of perfluoro-methyltetramethylenesulfur tetrafluoride were −6.1 ppm and −4.8 ppm respectively from external CF_3COOH.

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10) W. Autenrieth and A. Geyer, *Ber.*, **41**, 4249 (1908).