BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 51 (6), 1891—1892 (1978)

Electrochemical Fluorination of Thiols

Hajime Baba, Kazuo Kodaira, Shunji Nagase, and Takashi Abe

Government Industrial Research Institute, Nagoya, Hirate-machi, Kita-ku, Nagoya 462

(Received December 20, 1977)

Synopsis. Electrochemical fluorination of C_3 and C_4 thiols has been investigated. Perfluoroalkylsulfur pentafluoride derivatives including new compounds, together with fragmented fluorocarbons and sulfur hexafluoride, have been formed.

Our previous paper[1] showed that electrochemical fluorination of ethanethiol afforded a variety of fluoroalkyl sulfur compounds. As a continuation of this study, the electrochemical fluorination of C_3 and C_4 thiols including branched-chain compounds has been examined in the hope that the effects of branching on the products could be determined.

2-Propane- (I), 1-butane- (II), 2-methyl-1-propane- (III), 2-butane- (IV), and 2-methyl-2-propanethiols (V) have been subjected to the electrochemical fluorination. These were expected to yield perfluoroalkyl derivatives of sulfur hexafluoride, which have received considerable attention because of their unique inertness[2] and their usefulness as intermediates.[3]

The extensive breakdown of the thiols occurred, particularly in the carbon-sulfur bond during fluorination, and resulted in the formation of fluorocarbons and sulfur hexafluoride. Even so, a part of the starting materials was converted into the corresponding fully fluorinated analogs, perfluoroalkylsulfur pentafluorides. For example, II produced $CF_3(CF_2)_3SF_5$ (VI) in 12% yield. IV afforded a perfluoro compound which retained a sulfur pentafluoride group on the secondary carbon, $C_2F_5CF(CF_3)SF_5$[4] (VII), but the yield was poor (2%).

The physical constants and the ^{19}F and ^{1}H NMR spectral data of the isolated new compounds are shown in Table 1. These sulfur pentafluorides could be confirmed by their ^{19}F NMR spectra, which indicated the presence of two differently shielded types of fluorine nucleus bonded to the sulfur in the correct intensity ratio of 1: 4 in the regions expected.[5] The molecular ion peaks for these compounds were undetectable, but such characteristic ions as $[M-SF_5]$ and $[SF_3]$ were always found.

In the electrochemical fluorination of a tertiary thiol, V, the formation of the fully fluorinated analog of the starting material could not be confirmed. It yielded the entirely rearranged products, VI and $(CF_3)_2CFCF_2SF_5$ (VIII) in low yields ($\approx$2%), together with perfluorobutane (42%) and perfluoro (2-methylpropane) (4%).

The secondary thiols also gave isomerized derivatives as well as perfluorinated analogs of the starting materials; $CF_3CF_2CF_2SF_5$ (IX), $(CF_3)_2CFSF_5$ (X), and $C_2F_5CH_2SF_5$ (XI) were isolated in the fluorination of I, and VI and VII in the fluorination of IV. The other branched-chain thiol, III, produced VIII and the straight-chain compound VI. In these cases the amounts of the straight-chain perfluoro derivatives were higher than those of the branched-chain isomers, the yields of the former being up to 12%. The isomerization by the migration of a methyl or an ethyl group located at a branching site of the chain has been observed in the electrochemical fluorination of branched organic compounds, *e.g.* amines.[6]

The low yields of the fluorinated products from the thiols may be attributable partly to the instability of the thiols in anhydrous hydrogen fluoride.[7] Considerable amounts of polymeric tarry materials and elemental sulfur were always found as deposits on the electrodes and at the bottom of the electrolytic cell.

Experimental

Materials and Apparatus. The thiols used were commercial chemicals. II (97%) contained a small amount of III. The others were more than 98% pure. The electrolytic fluorination apparatus[8] and operating procedures[1] were similar to the ones described previously. The mass spectra were recorded on a Hitachi RMU-7 instrument at 70 eV, the ^{19}F NMR spectra on a Hitachi R-20B instrument at 56.4 MHz, and the ^{1}H NMR spectra on a Hitachi R-22 instrument at 90 MHz.

Fluorination of 2-Propanethiol (I). I (25.0 g, 0.328 mol) was added to electrochemically purified anhydrous hydrogen fluoride (400 ml) in the cell. The resulting solution was electrolyzed under the following conditions: anodic current density, 2.6 A/dm^2 (effective surface area of anodes, 770 dm^2); cell voltage, 4.7—6.1 V; cell temperature, 8—10 °C; electricity supplied, 227 A h (670 min); helium flow rate, 60 ml/min.

The products collected in a series of cold traps immersed in ice and in liquid nitrogen were combined (71.3 g) and distilled into four fractions, and each fraction was then subjected to gas-chromatographic analysis (column: 2 m × 3 mm, silica gel; 4 m × 3 mm, Daifl oil 3 (20%) on Chromosorb P-AW). The following compounds were obtained (the compositions were calculated on the basis of the chromatographic peak areas): C_1 and C_2 fluorocarbons (0.9 g), SF_6 (18.8 g), C_3F_8 (30.1 g, 48.8%), n-C_4F_{10} (0.1 g), $CHF_2C_2F_5$ (1.1 g), $(CF_3)_2CHF$ (1.2 g), $CH_2FC_2F_5$ (6.4 g), $C_2H_5CF_3$ (0.9 g), $C_2F_5SF_5$ (0.2 g), IX (3.3 g, 3.4%), X (1.7 g, 1.8%), XI (0.8 g, 0.9%), others (unidentified complex mixtures, 5.6 g).

X, MS: *m/e* 169 $[M-SF_5]$, 131 $[C_3F_5]$, 127 $[SF_5]$, 119 $[C_2F_5]$, 100 $[C_2F_4]$, 89 $[SF_3]$, 70 $[SF_2]$, 69 $[CF_3]$. Found: C, 12.19; F, 76.5%. Calcd for $C_3F_{12}S$: C, 12.17; F, 77.0%. XI, MS: *m/e* 241 $[M-F]$, 191 $[M-CF_3]$, 133 $[M-SF_5]$, 131 $[C_3F_5]$, 127 $[SF_5]$, 119 $[C_2F_5]$, 113 $[C_3HF_4]$, 100 $[C_2F_4]$, 89 $[SF_3]$, 83 $[C_2H_2F_3]$, SF_2 [70], 69 $[CF_3]$. Found: C, 14.02; H, 0.84; F, 72.4%. Calcd for $C_3H_2F_{10}S$: C, 13.85; H, 0.78; F, 73.0%.

Fluorination of 1-Butanethiol (II). II (20.6 g, 0.288 mol) was fluorinated under the following conditions: 2.9 A/dm^2, 5.8—8.0 V, 14—15 °C, 151 A h (400 min), helium 60 ml/min. The following compounds were obtained: C_1, C_2, and C_3 fluorocarbons (0.9 g), SF_6 (5.9 g), CF_3SF_5 (0.2 g), $(CF_3)_3CF$ (0.8 g), n-C_4F_{10} (6.9 g, 10.6%), $C_2F_5SF_5$ (0.4 g), $(CF_3)_3CH$

Table 1. Fluoroalkyl sulfur compounds

Compound	Source[a)]	Bp[b)] (°C)	n_D^{20}	^{19}F and H^1 NMR spectral data[c),d)] Chemical shifts, ppm	Coupling constants, Hz
$(CF_3)_2CFSF_5$	I	43.3	<1.28	$(CF_3{}^a)_2CF^tSF_5$ F^a 72.2, F^t 150.5, SF_{eq} −55.8, SF_{ax} −65.4	F^a–SF_{eq} 12.8, F^a–F^t 6.2, SF_{ax}–F^t 3.3, SF_{ax}–F^a 1.5, SF_{ax}–SF_{eq} 140.6
$C_2F_5CH_2SF_5$	I	60.0	<1.28	$CF_3{}^aCF_2{}^bCH_2SF_5$ F^a 86.2, F^b 120.1 SF_{eq} −73.1, SF_{ax} −75.5 H 4.0	SF_{ax}–SF_{eq} 128 H–F^b 16, H–SF_{eq} 7
$(CF_3)_2CFCF_2SF_5$	III V	69.0	<1.28	$(CF_3{}^a)_2CF^tCF_2{}^bSF_5$ F^a 72.5, F^b 87.9, F^t 183.2 SF_{eq} −44.2, SF_{ax} −62.6	F^a–F^b 10.6, F^a–SF_{eq} 5.4, F^a–F^t 5.2, SF_{ax}–F^t 1.8, SF_{ax}–F^b 5.0, SF_{ax}–SF_{eq} 142.7
$C_2F_5CF(CF_3)SF_5$	IV	71.0	<1.28	$CF_3{}^aCF_2{}^bCF^t(CF_3{}^c)SF_5$ F^a 79.9, F^b 117.9, F^c 70.6 F^t 147.1, SF_{eq} −58.2, SF_{ax} −65.1	F^a–SF_{eq} 9.3, F^a–F^t 6.2, F^a–F^c 3.1, SF_{ax}–SF_{eq} 139.2

a) I: 2-Propanethiol, III: 2-methyl-1-propanethiol, IV: 2-butanethiol, V: 2-methyl-2-propanethiol. b) Recorded, uncorrected, at atmospheric pressure. c) CCl_4 solution. Chemical shifts are in δ values with respect to CCl_3F for ^{19}F and to TMS for ^1H as internal references. d) SF_{eq} and SF_{ax} indicate equatorial and axial fluorine atoms respectively.

(0.1 g), $CF_3CH_2C_2F_5$ (0.4 g), VI (9.7 g, 12.3%), others (1.0 g).

Fluorination of 2-Methyl-1-propanethiol (III). III (25.0 g, 0.277 mol) was fluorinated; 3.0 A/dm², 4.8—6.0 V, 10—11 °C, 174 A h (455 min), helium 60 ml/min. The following compounds were obtained: C_1, C_2, and C_3 fluorocarbons (0.3 g), SF_6 (7.6 g), $(CF_3)_3CF$ (2.3 g, 3.5%), n-C_4F_{10} (5.5 g, 8.4%), $(CF_3)_2C{=}CF_2$ (0.1 g), $CF_3CHFC_2F_5$ (0.2 g), $(CF_3)_3CH$ (0.2 g), $CF_3CH_2C_2F_5$ (0.2 g), IX (0.4 g), VIII (2.4 g, 2.5%), VI (11.7 g, 12.2%), others (0.6 g).

VIII, MS: m/e 219 [$M-SF_5$], 150 [C_3F_6], 131 [C_3F_5], 127 [SF_5], 119 [C_2F_5], 100 [C_2F_4], 89 [SF_3], 70 [SF_2], 69 [CF_3]. Found: C, 13.62; F, 76.7%. Calcd for $C_4F_{14}S$: C, 13.88; F, 76.9%.

Fluorination of 2-Butanethiol (IV). IV (25.0 g, 0.277 mol) was fluorinated; 3.1 A/dm², 4.8—7.5 V, 9—11 °C, 203 A h (510 min), helium 60 ml/min. The following compounds were obtained: C_1, C_2, and C_3 fluorocarbons (2.3 g), SF_6 (15.0 g), $(CF_3)_3CF$ (1.6 g), n-C_4F_{10} (32.3 g, 48.9%), $CF_3CHFC_2F_5$ (0.6 g), $(CF_3)_3CH$ (0.2 g), $CF_3CH_2C_2F_5$ (0.6 g), IX (0.2 g), VI (5.0 g, 5.3%), VII (1.9 g, 2.0%), $[CF_3(CF_2)_3]_2SF_4$ (0.1 g), others (1.5 g).

VII,[4)] MS: m/e 219 [$M-SF_5$], 150 [C_3F_6], 131 [C_3F_5], 127 [SF_5], 100 [C_2F_4], 93 [C_3F_3], 89 [SF_3], 70 [SF_2], 69 [CF_3]. Found: C, 13.70; F, 77.1%. Calcd for $C_4F_{14}S$: C, 13.88; F, 76.9%.

Fluorination of 2-Methyl-2-propanethiol (V). V (24.0 g, 0.266 mol) was fluorinated; 3.2 A/dm², 5.1—6.6 V, 10—12 °C, 172 A h (420 min), helium 60 ml/min. The following compounds were obtained: C_1, C_2, and C_3 fluorocarbons (5.3 g), SF_6 (6.2 g), n-C_4F_{10} (26.4 g, 41.8%), $(CF_3)_3CF$ (2.6 g, 4.1%), $CF_3CHFC_2F_5$ (0.9 g), $CHF_2C_3F_7$ (0.2 g), $(CF_3)_3CH$ (0.4 g), $CF_3CH_2C_2F_5$ (2.9 g), n-C_5F_{12} (0.8 g), IX (0.1 g), VI (2.0 g, 2.2%), VIII (0.6 g, 0.7%), others (6.0 g).

References

1) H. Baba, K. Kodaira, S. Nagase, and T. Abe, *Bull. Chem. Soc. Jpn.*, **50**, 2809 (1977).

2) For example, Shin-Liang Yu, and J. M. Shreeve, *J. Fluorine Chem.*, **6**, 259 (1975).

3) Dow Corning Co., Fr. 1512068 (1967); L. A. Loree, U. S. 3456024 (1969).

4) The formula is listed in Ref. 3.

5) a) N. Muller, P. C. Lauterbur, and G. F. Svatos, *J. Am. Chem. Soc.*, **79**, 1043 (1957); b) M. T. Rogers and J. D. Graham, *ibid.*, **84**, 3666 (1962).

6) a) T. C. Simmons, F. W. Hoffmann, R. B. Beck, H. V. Holler, T. Katz, R. J. Koshar, E. R. Larsen, J. E. Mulvaney, K. E. Paulson, F. E. Rogers, B. Singleton, and R. E. Sparks, *J. Am. Chem. Soc.*, **79**, 3429 (1957); b) V. S. Plashkin, L. N. Pushkina, and S. V. Sokolov, *Zh. Org. Khim.*, **10**, 1215 (1974); c) K. Omori, S. Nagase, H. Baba, K. Kodaira, and T. Abe, *J. Fluorine Chem.*, **9**, 279 (1977).

7) J. H. Simons, "Fluorine Chemistry," Vol. 1, ed by J. H. Simons, Academic Press, New York (1950), p. 239.

8) S. Nagase, H. Baba, and T. Abe, *Bull. Chem. Soc. Jpn.*, **40**, 2358 (1967).