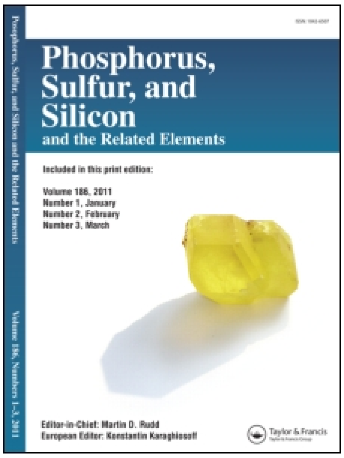

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Dialkylamido Sulfoxylic Acid Fluorides, I: Synthesis and Reactions with Olefins

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Dialkylamido Sulfoxylic Acid Fluorides, I: Synthesis and Reactions with Olefins

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The reaction of potassium fluoride with the corresponding acid chlorides results in the formation of dialkylamido sulfoxylic acid fluorides Alk_2N*-S-F. Stereo- and regioselectivity of dimethylamido and diisopropylamido sulfoxylic acid fluorides addition reactions to the C,C double bond in cyclohexene, 3,4-dihydro-2H-pyrane, and vinyl ethyl ether has been investigated. This reaction is a convenient approach to the β-fluoroalkyl sulfenic acid derivatives.*

Keywords Alkenes; fluorides of dialkylamido sulfoxylic acids; fluorinating reagents; β-fluoroalkyl sulfenic acid

INTRODUCTION

Organic compounds of four- and six-valent sulfur with sulfur-fluorine bonds (sulfinic and sulfonic acids fluorides, S^{IV} and S^{VI} fluorosulfuranes) are well studied and widely used in organic synthesis. Another situation is observed for the organic compounds of two-valent sulfur with a sulfur fluorine bond. Arenesulfinic acid fluorides Ar-S-F are practically unknown. Perfluoroalkyl sulfenic acid fluorides Alk_F-S-F are unstable, and their disproportion results in formation of trifluorosulfuranes.[1–4]

We had shown earlier in the course of investigations on the properties of *S*-organyl-*S*-(dialkylamino)difluorosulfuranes that *S*-(benzthiazolyl-2)-*S*-(dialkylamino)difluorosulfurane decomposes to

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Dedicated to Professor Marian Mikołajczyk, CBMiM PAN in Łódź, Poland, on the occasion of his 70th birthday.

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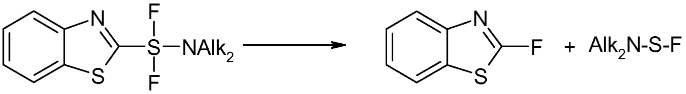
form 2-fluorobenzthiazole and dialkylamido sulfoxylic fluorides (Alk_2N-S-F, Alk = CH_3, C_2H_5; Alk_2 = $O(CH_2)_4$, $(CH_2)_5$)[5]; Scheme 1).



SCHEME 1

The synthesis of hydrolytically unstable compounds of this class was described,[6–8] but their thermal stability and chemical properties have not been studied.

The aim of the presented work is the development of a synthetic method as well as investigation of the thermal stability and chemical properties of dialkylamido sulfoxylic acid fluorides.

RESULTS AND DISCUSSION

We have shown that the reaction of morpholino sulfoxylic acid chloride and potassium fluoride in acetonitrile results in the formation of the corresponding morpholino sulfoxylic acid fluoride.[5] The detailed investigation of this interaction has shown that this approach is general and can be used to obtain also the dialkylamido sulfoxylic acid fluorides **1a**,**b** (Scheme 2).

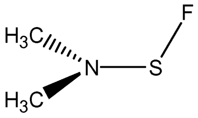
$$\mathrm{Alk_2N{-}S{-}Cl} + \mathrm{KF} \xrightarrow{\mathrm{CH_3CN}} \underset{\mathbf{1\ a,b}}{\mathrm{Alk_2N{-}S{-}F}} + \mathrm{KCl}$$

1: **a**) Alk = Me, **b**) *i*-Pr

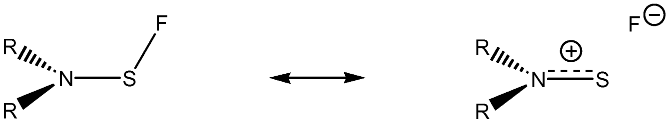
SCHEME 2

The reaction proceeds at room temperature for 16 h. We have not succeeded in isolating fluorides **1a**,**b** from the reaction mixture, as they decompose upon solvent evaporation. However, they can be kept under exclusion of air and moisture as acetonitrile solution for several weeks.

The peculiarity of the fluorides **1a**,**b** is a ^{19}F NMR resonance at high field (–163.7 for **1a**, –153.5 for **1b**), which is obviously different from the ^{19}F chemical shifts typical for derivatives of sulfuric and sulfurous acids Alk_2NSOF and Alk_2NSO_2F (20–70 ppm).[9] It may be assumed that this fact is evidence of a considerable contribution of the mesomeric structure **B** (Figure 1) to the general electronic distribution in the molecules and, consequently, a high mobility of the fluorine atoms.



1a

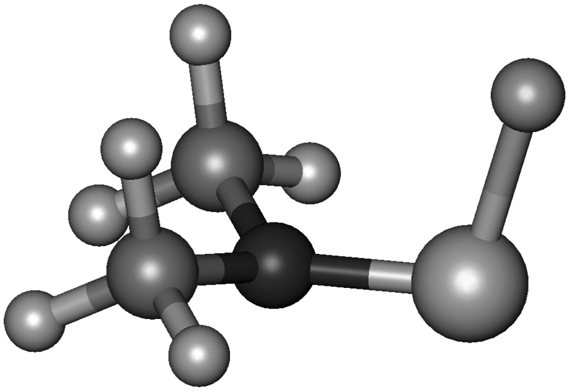


A **B**

FIGURE 1 Mesomeric structures of dialkylamino sulfoxylic acid fluorides.

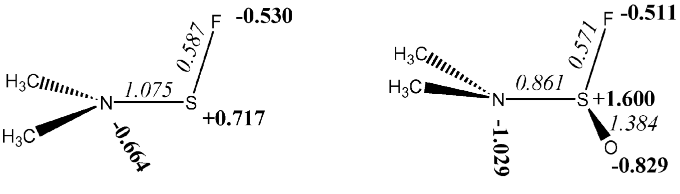
The structure of **1a** optimized at the MP2(fc)/6–311+G** level of theory is shown in Figure 2. A detailed description of the calculation methods is given in the Experimental section. Geometry optimization without any symmetry restrictions leads to the C_s symmetrical structure.

The specific feature of **1a** is the practically trigonal planar configuration of the nitrogen atom (sum of angles 353.6°) and the shortened (1.616Å) N—S bond. (For comparison, the N—S bond length calculated within the same approximation for the model compound H_2N-S-H is



1a

FIGURE 2 Calculated (MP2(fc)/6–311+G**) structure of **1a.** Most important structural parameters: N-S 1.616 Å; S-F 1.730 Å; ∠NSF 105.3°; ∠CNS 120.1°; ∠CNC 113.5°; ∠NSF 75.0°.



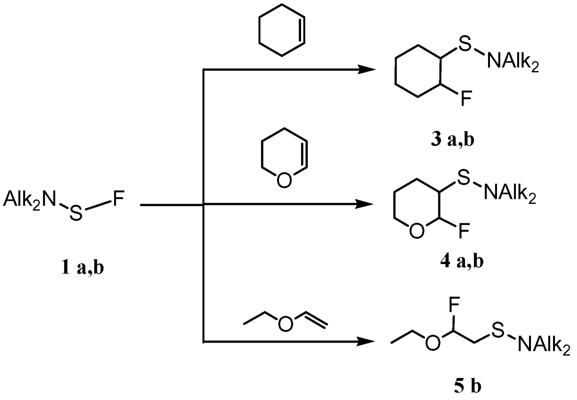
1a **2**

FIGURE 3 Charge distribution and Wiberg indexes of compounds **1a** and **2**.

found to be 1.708 Å, and the sum of the angles at nitrogen is 337.9°.) On the other hand, the S-F bond length exceeds the corresponding value found for Me-S-F (1.668 Å). Thus, some structural and spectral properties are present, which make it possible to suggest a significant contribution of the mesomeric form **B** to the structure of the molecules **1a**,**b.** However, some other facts should also be taken into account. The analysis of the charge distribution performed within the NBO approach shows that the N-S bond is highly polarized and hence possesses an ylidic character. Important evidence to this interpretation is an insignificant increase of the Wiberg index for the N-S bond compared to the formally single bond. As expected, a significant negative charge is localized at the fluorine atom; however its magnitude (–0.53) does not directly prove the existence of **1a**,**b** as the tight ion pair **B**. Thus, the exceeded charge at the fluorine atom calculated for the sulfinic acid derivative **2** is even larger (–0.56), whereas the δ^{19}F values differ strongly from those found for **1a**,**b** (Figure 3). Therefore, the charge distribution itself is not the main reason of the strong shielding of the fluorine nuclei found for **1a**,**b.** The calculation results for the synthesized fluorides of the dialkylamino sulfoxylic acids and related compounds as well as the character of the influence of their electronic structure on the spectral characteristic will be considered in one of our future publications.

The chemical properties of the dialkylamido sulfoxylic acid fluorides **1a**,**b** have been studied by taking their reaction with unsaturated compounds as an example. We have chosen cyclohexene, 3,4-dihydro-2*H*-pyrane, and vinyl ethyl ether as substrates. In every case, the reaction was performed in solution of anhydrous acetonitrile with cooling in an ice bath (the reaction is exothermic). The products were purified by distillation in high vacuum; partial tarring was observed (Scheme 3).

We attribute to the compound **3a** *trans*-configuration with equatorial position of the fluorine and sulfur atoms **(eFeS)**. This is confirmed

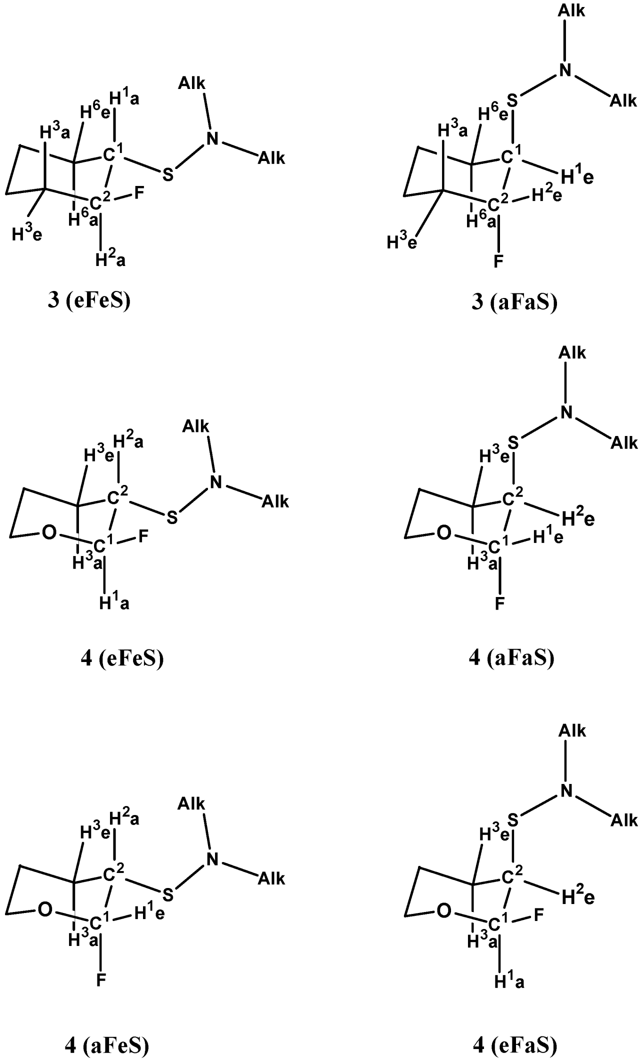


1, 3, 4, 5: Alk = **a**) Me, **b**) *i*-Pr

SCHEME 3

by the values of vicinal coupling constants $^{3}J_{H^{1}H^{2}}$ (9 Hz) and $^{3}J_{FH^{1}}$ (10 Hz). Optimization of all possible structures for **3a** shows that torsion angles $\angle H^{1}C^{1}C^{2}H^{2}$ and $FC^{2}C^{1}H^{1}$ for the conformation **3a (eFeS)** (Figure 4) are 170.4° and –54.4°, respectively, which agrees with the experimental values on the basis of Karplus dependences for the values of the corresponding coupling constants.[10,11]

It should be mentioned that only regioisomers **4** and **5**, in which the fluorine atom is bonded to the α-carbon atom, were formed in the case of 3,4-dihydro-2*H*-pyrane or vinyl ethyl ether. Compound **4a** is obviously a *trans* isomer with conformation **(aFaS)** (Figure 4). This is confirmed by the small value of the vicinal coupling constant $^{3}J_{FH^{2}}$ (6.0 Hz). The approximate value of the torsion angle $\angle FC^{1}C^{2}H^{2}$ corresponding to this coupling constant and obtained by Karplus equation[11] is about 58°. For the structure **4a (aFaS)**, optimized at the B3LYP/6-311++G** level of theory (Figure 5), the mentioned angle is 65.3°. This assignment agrees with the values of full energies calculated for the corresponding isomers [**4a (aFaS)** is characterized by lower full energy than **4a (eFeS)**, Table I]. In addition the preferable equatorial position of the substituents in cyclohexanes and axial in tetrahydropyranes (in consequence of the so called anomeric effect) is well documented in the literature.[11] Together with the main product **4a (aFaS)**, the *cis*-isomer with suppositional conformation **4a (aFeS)** is formed as a minor product (about 9%) (Figure 4). The calculated full energy of the last one is lower than in case of conformation **4a (eFaS),** obviously due to the mentioned above anomeric effect. The main argument in favor



3 (eFeS) **3 (aFaS)**

4 (eFeS) **4 (aFaS)**

4 (aFeS) **4 (eFaS)**

FIGURE 4 Conformational and stereoisomers of compounds **3** and **4**.

of this structure is the high value of the vicinal coupling constant $^{3}J_{\mathrm{FH}^2}$ (30.6 Hz), which should correspond to a value of the torsion angle $\angle \mathrm{FC}^1\mathrm{C}^2\mathrm{H}^2$close to 180°.[11] The mentioned value for the optimized structure **4a (aFeS)** is 171.3° (Figure 5). The absolute value of the constant $^{3}J_{\mathrm{H}^1\mathrm{H}^2}$ (2.0 Hz) fits well to the theoretically calculated value of the

TABLE I Total Energy (E), ZPE Correction, Corrected Energy Values (Hartree), Lowest Vibration Frequencies Calculated for Different Structures, and Relative Energy Magnitudes (kcal/mol) Calculated (B3LYP/6–311++G) for 3a and 4a**

	Conformation[a]	Total Energy, E	ZPE correction	E+ZPE	ν, cm^{-1}	ΔE, kcal/mol[b]
trans-**3a**	**(aFaS)**	–867.416871	0.235036	–867.181835	23.1	0.6
trans-**3a**	**(eFeS)**	–867.417760	0.234906	–867.182854	23.2	**0.0**
cis-**3a**	**(aFeS)**	–867.415587	0.234904	–867.180683	25.1	1.4
cis-**3a**	**(eFaS)**	–867.416087	0.234841	–867.181246	28.2	**1.0**
trans-**4a**	**(aFaS)**	–903.329231	0.211276	–903.117955	23.3	**0.2**
trans-**4a**	**(eFeS)**	–903.326538	0.211037	–903.115501	23.2	1.7
cis-**4a**	**(aFeS)**	–903.322612	0.210911	–903.111701	21.0	**0.0**
cis-**4a**	**(eFaS)**	–903.329442	0.211227	–903.118215	26.0	4.1

[a] Conformations with the NMe_2 group oriented towards the ring possess higher energies and are not considered here.

[b] Bold marked values are referred to the most favored conformations for the *cis*- and *trans*-isomers.

angle $\angle H^1C^1C^2H^2$ (54.2°) and its approximate evaluation by Karplus equation.

It should be mentioned that in case of the compound **4b,** a small quantity of the *cis*-isomer is formed (< 1%).

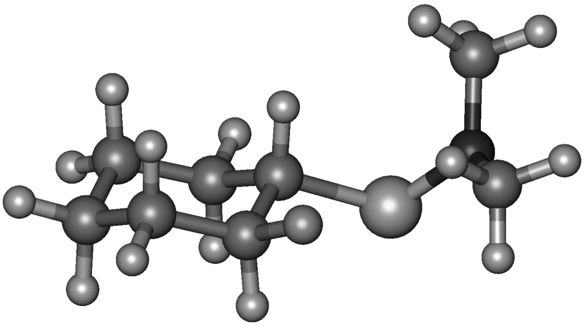
The action of gaseous hydrogen chloride on 2-fluorocyclohexyl sulfenic acid diisopropyl amide **3b** leads to the cleavage of the S-N bond and formation of 2-fluorocyclohexyl sulfenic acid chloride **6**. Compound **6** is a representative of the alkylsulfenyl chlorides of a new type, as it contains a fluorine atom at the β-carbon atom.

In conclusion, we propose new reagents that allow the introduction fluorine atoms in molecules of unsaturated aliphatic compounds forming stereo- and regioselectively β-fluoroalkane sulfenic acid derivatives.

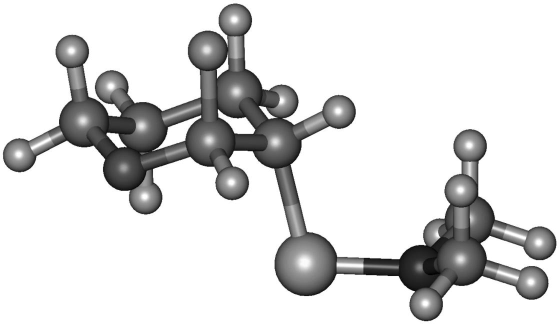
EXPERIMENTAL

Reagents and Materials

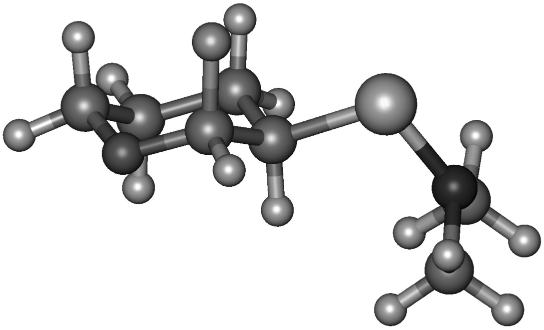
Reactions with compounds, sensitive to air and moisture, were conducted in glassware and flame dried in a flow of dry argon using anhydrous solvents in an atmosphere of dried argon. ^1H and ^{19}F NMR spectra were recorded with a Varian VRX-300 spectrometer operating at 299.9 MHz and 188.1 MHz, respectively. ^{13}C NMR spectra were obtained with a Bruker Avance 400 spectrometer operating at 100.62 MHz. Chemical shifts of the nuclei ^1H and ^{13}C are given in δ values



3a (eFeS)

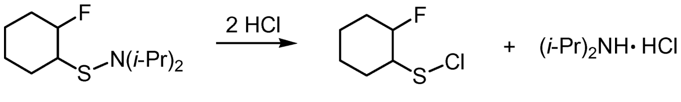


4a (aFaS)



4a (aFeS)

FIGURE 5 Calculated (B3LYP/6-311++G**) most stable conformations of the compounds **3à (eFeS)**, **4à (àFàS)**, and **4à (àFåS)**. The most important structural parameters (bond lengths in Å, angles in °): N-S 1.703, 1.713, 1.713; C^1-F 1.414, 1.424, 1.415; C^2-S 1.873, 1.877, 1.868; NSC^2 109.6, 105.3, 105.6; $H^1C^1C^2H^2$ 170.4, 65.3, 54.2; $FC^1C^2H^2$ 54.4, 51.2, 171.3, respectively.



3 b **6**

SCHEME 4

relatively to TMS as an internal standard. C_6F_6 ($\delta^{19}F$ = –162.9 ppm with respect to $CFCl_3$) was used as an internal standard. "Spray-dried" potassium fluoride of 99% purity was used for the reactions.

Details of Calculations

The structures were optimized using the GAUSSIAN-03 program set[12] at the DFT (B3LYP[13]) and MP2 (with the frozen core approximation) levels of theory. For the former case, the three-parameter hybrid functional including Lee, Yang, and Parr[14] and VWN5[15] functionals was used. The geometry optimization was performed using 6-311+G** (for the calculations at the MP2 level of approximation) or 6-311++G** (for the DFT calculations) basis sets. Within the GAUSSIAN package, the default usage of these basis sets meant Pople's 6-311G basis sets[16] for hydrogen and second period atoms (C, N, O, F) and McLean-Chandler basis set[17] for sulfur, augmented with the corresponding polarization and diffuse Gauss functions. In order to make sure that all the calculated structures corresponded to the local minima in energy, we performed the vibration frequency analyses calculating analytically the first and second derivatives. The optimized structures are presented using the VMD program.[18]

Syntheses

Synthesis of Compounds 3a,b, 4a,b, and 5b: General Procedure

Anhydrous KF (4.5 g, 77.4 mmol), 15 mL of acetonitrile, and dialkylamino sulfoxylic acid chloride (25.8 mmol) were placed into a flask with a magnetic mixer anchor. The reaction mixture was stirred at room temperature for 16 h. Volatile products were evaporated in vacuum (0.04 Torr) into a trap cooled by liquid nitrogen. The content of the trap (dialkylamido sulfoxylic acid fluoride and acetonitrile) was warmed to 0°Ñ, and alkene (2.12 g, 25.8 mmol) was added to the mixture with stirring during 5 min. The reaction mixture was warmed to room temperature during 1 h. The solvent was evaporated in vacuum (0.04 Torr), and the crude oily products were purified by vacuum distillation. The yields of the crude products in all cases are close to quantitative based on ^{1}H and ^{19}F NMR data.

2-Fluorocyclohexyl Sulfenic Acid Dimethylamide (3a)

Yield: 31.2%, b.p. 50–52°C/0.04 Torr; ^{1}H NMR ($CDCl_3$/TMS): $\delta = 1.3$ (m, 2H, cyclohexyl), 1.45–1.74 (m, 3H, cyclohexyl), 1.73 (m, 1H, cyclohexyl), 2.1 (m, 2H, cyclohexyl), 2.74 (s, 6H, CH_3), 2.85 (dddd, $^3J_{HF} = 10.0$ Hz, $^3J_{H6a} = 8.7$ Hz, $^3J_{H2a} = 8.7$ Hz, $^3J_{H6e} = 4.1$ Hz, 1H, CHS), 4.44 (dddd, 1H, $^2J_{HF} = 48.6$ Hz, $^3J_{H1a} = 8.9$ Hz, $^3J_{H3a} = 8.9$ Hz; $^3J_{H3e} = 4.2$ Hz, CHF); ^{19}F NMR ($CDCl_3/C_6F_6$): $\delta = -171.07$ (d, $J = 45.3$ Hz);^{13}C NMR ($CDCl_3$): $\delta = 92.7$ (d, $J = 176.0$ Hz, C-2), 50.4 (Me), 50.2 (d, $J = 24.8$ Hz, C-1), 31.7 (d, $J = 19.8$ Hz, C-3), 30.0 (d, $J = 4.4$ Hz, C-6), 25.0 (C-5), 23.3 (d, $J = 8.7$ Hz, C-4). Calcd for $C_8H_{16}FNS$ (177.28): C, 54.20; H, 9.10; F, 10.72; N, 7.90; S, 18.09. Found: C, 54.00; H, 8.85; F, 10.84; N, 7.78; S, 18.02%.

2-Fluorocyclohexyl Sulfenic Acid Diisopropylamide (3b)

Yield: 62.6%, b.p. 67–70°C / 0.03 Torr; ^{1}H NMR ($CDCl_3$/TMS): $\delta = 1.09$ (dd, $J = 6.6$ Hz, 2.1 Hz, 12H, CH_3), 1.3–1.8 (m, 6H, cyclohexyl), 2.0–2.2 (m, 2H, cyclohexyl), 2.71 (dddd, $^3J_{H2a} = 9.7$ Hz, $^3J_{HF} = 9.5$ Hz, $^3J_{H6a} = 9.5$ Hz, $^3J_{H6e} = 4.5$ Hz, 1H, CHS), 3.22 (sept, $J = 6.5$ Hz, 2H, CH), 4.49 (dddd, $^2J_{HF} = 48.6$ Hz, $^3J_{H1a} = 7.8$ Hz, $^3J_{H3a} = 7.8$ Hz; $^3J_{H3e} = 3.9$ Hz, 1H, CHF);^{19}F NMR ($CDCl_3/C_6F_6$): $\delta = -173.1$ (d, $J = 48.7$ Hz);^{13}C NMR ($CDCl_3$): $\delta = 93.2$ (d, $J = 175.5$ Hz, C-2), 55.6 (d, $J = 16.4$ Hz, C-1), 54.1 (CH), 31.0 (d, $J = 19.8$ Hz, C-3), 28.8 (d, $J = 3.8$ Hz, C-6), 24.3 (C-5), 23.8 (CH_3), 22.8 (d, $J = 8.2$ Hz, C-4). Calcd for $C_{12}H_{24}FNS$ (233.37): C, 61.75; H, 10.36; F, 8.14; N, 6.00; S, 13.74. Found: C, 62.01; H, 10.33; F, 7.76; N, 6.12; S, 14.12%.

2-Fluorotetrahydro-2H-pyrane-3-sulfenic Acid Diisopropylamide (4b)

Yield: 33%, b.p. 65–67°C / 0.03 Torr;^{1}H NMR ($CDCl_3$/TMS): $\delta = 1.08$ (d, $J = 6.6$ Hz, 12H, CH_3), 1.42 (m, 1H, $C\underline{H}_2CHS$), 1.85 (t, $J = 15.3$ Hz, 2H, $CH_2C\underline{H}_2CH_2$), 2.12 (m, 1H, $C\underline{H}_2CHS$), 2.82 (s, 1H, CHS), 3.20 (sept, $J = 6.5$ Hz, 2H, CH), 3.70 (m, 1H, CH_2O), 3.91 (td, $J = 11.1$ Hz, 2.1 Hz, 1H, CH_2O), 5.67 (d, $^2J_{HF} = 52.8$ Hz, 1H, CHF); ^{19}F NMR ($CDCl_3/C_6F_6$): $\delta = -129.3$ (d, $J = 52.5$ Hz); ^{13}C NMR ($CDCl_3$): $\delta = 108.3$ (d, $J = 220.5$ Hz, C-1), 62.1 (d, $J = 3.2$ Hz, C-5), 55.1 (CH), 51.0 (d, $J = 23.9$ Hz, C-2), 23.4 (CH_3), 21.8 (C-3), 21.1 (C-4). Calcd for $C_{11}H_{22}FNOS$ (235.36): C, 56.13; H, 9.42; F, 8.07; N, 5.95; S, 13.62. Found: C, 56.20; H, 9.50; F, 7.75; N, 6.23; S, 13.59%.

2-Ethoxy-2-Fluoroethyl Sulfenic Acid Diisopropylamide (5b)

Yield: 21%, b.p. 50–55°C / 0.07 Torr;^{1}H NMR (CDCl$_3$/TMS): $\delta = 1.10$ (d, $J = 6.6$ Hz, 12H, $C\underline{H}_3CH$), 1.25 (t, $J = 6.9$ Hz, 3H, CH_3), 2.78 (m, 1H, SCH_2), 2.82 (m, 1H, SCH_2), 3.21 (sept, $J = 6.5$ Hz, 2H, CH), 3.78 (d, $J = 71.1$ Hz, OCH_2), 5.41 (dt, $J = 66.9$ Hz, 5.25 Hz, -CHF-);^{19}F NMR ($CDCl_3/C_6F_6$): $\delta = -121.64$ (dt, $J = 66.0$ Hz, 14.9 Hz); ^{13}C NMR ($CDCl_3$): $\delta = 111.6$ (d, $J = 215.7$ Hz, CF), 65.8 (CH_2O), 55.9 (CH), 47.3 (d, $J = 22.6$ Hz, CH_2S), 23.7 ($CHC\underline{H}_3$), 15.4 ($CH_2C\underline{H}_3$). Calcd for $C_{10}H_{22}FNOS$ (223.35): C, 53.77; H, 9.93; F, 8.51; N, 6.27; S, 14.36. Found: C, 53.68; H, 9.93; F, 8.15; N, 6.76; S, 14.38%.

Trans-2-fluorotetrahydro-2H-pyrane-3-sulfenic Acid Dimethylamide (4a, aFaS)

Yield: 43%, b.p. 57–60°C / 0.04 Torr; ^{1}H NMR (CDCl$_3$/TMS): $\delta = 1.47$ (m, 1H, $C\underline{H}_2CHS$), 1.78 (m, 2H, $CH_2C\underline{H}_2CH_2$), 2.23 (m, 1H, $C\underline{H}_2CHS$), 2.72 (s, 6H, CH_3), 3.21 (s, 1H, CHS), 3.71 (m, 1H, CH_2O), 3.94 (m, 1H, CH_2O), 5,63 (dd, $^2J_{HF} = 52.8$ Hz, $^3J_{H2e} = 5.8$ Hz, 1H, CHF); ^{19}F NMR ($CDCl_3/C_6F_6$): $\delta = -127.07$ (dd, $J = 52.5$ Hz, 6.0 Hz);^{13}C NMR ($CDCl_3$): $\delta = 108.6$ (d, $J = 222.6$ Hz, C-1), 62.3 (d, $J = 3.3$ Hz, C-5), 49.6 (Me), 43.7 (d, $J = 25.2$ Hz, C-2), 23.3 (C-3), 21.6 (C-4). Calcd for $C_7H_{14}FNOS$ (179.26): C, 46.90; H, 7.87; F, 10.60; S, 17.89. Found: C, 46.84; H, 7.76; F, 10.56; S, 17.66%.

Cis-2-fluorotetrahydro-2H-pyrane-3-sulfenic Acid Dimethylamide (4a, aFeS)

^{19}F NMR ($CDCl_3/C_6F_6$): $\delta = -146.9$ (dd, $^2J_{H1e} = 51.4$ Hz, $^3J_{H2a} = 30.6$ Hz);^{13}C NMR ($CDCl_3$): $\delta = 107.6$ (d, $J = 220.2$ Hz, C-1), 61.6 (d, $J = 3.7$ Hz, C-5), 49.9 (Me), 46.1 (d, $J = 27.6$ Hz, C-2), 25.6 (C-3), 23.9 (C-4).

2-Fluorocyclohexyl Sulfoxylic Acid Chloride (6)

Hydrogen chloride (6.24 g, 171.2 mmol) is passed into a solution of 2-fluorocyclohexyl sulfenic acid diisopropylamide **3b** (2.0 g, 8.56 mmol) in diethyl ether (20 mL). The colorless crystalline precipitate was filtered and the filtrate was evaporated in vacuum. 2-Fluorocyclohexyl sulfenic acid chloride **6** remained in the residue and was purified by distillation in vacuum. Yield: 81%, b.p. 55°C / 0.07 Torr; ^{1}H NMR (CDCl$_3$/TMS): $\delta =$ 1.3–1.4 (m, 2H, cyclohexyl), 1.5–1.85 (m, 4H, cyclohexyl), 2.1–2.3 (m, 2H, cyclohexyl), 3.05 (dddd, $^3J_F = 10.7$ Hz, $^3J_{H2a} = 8.5$ Hz; $^3J_{H6a} = 8.0$ Hz; $^3J_{H6e} = 4.2$ Hz, 1H, CHS), 4.5 (dddd, $^2J_{HF} = 48.0$ Hz, $^3J_{H1a} = 9.5$ Hz, $^3J_{H3a} = 9.5$ Hz, $^3J_{H3e} = 4.7$ Hz, 1H, CHF).^{19}F NMR ($CDCl_3/C_6F_6$): $\delta = -173.1$ (d, $J = 48.7$ Hz). Calcd for $C_6H_{10}ClFS$ (168,66): C, 42.73; H, 5.98; F, 11.26; S, 19.01; Cl, 21.02. Found: C, 42.70; H, 5.99; F, 9.56; S, 19.17; Cl, 21.08%.

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