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Preparation of *N*,*N*-dialkyl-*N′*-perfluoroalkanesulfonylformamidines $R_fSO_2N{=}CHNR_2$ via Vilsmeier reagents

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Abstract

Treatment of sodium perfluoroalkanesulfonylamides R_fSO_2NHNa with Vilsmeier reagents $[YCH{=}^+NR_2]Cl^-$ ($Y \equiv OP(O)Cl_2, OS(O)Cl$) give the title compounds $R_fSO_2N{=}CHNR_2$ in good yields. The molecular structure of $I(CF_2)_2O(CF_2)_2SO_2N{=}CHNMe_2$ is presented. © 1997 Elsevier Science S.A.

Keywords: Vilsmeier reagents; Sodium perfluoroalkanesulfonylamides; *N*,*N*-dialkyl-*N′*-perfluoroalkanesulfonylformamidines

1. Introduction

Vilsmeier reagents are widely used in organic synthesis, especially in the preparation of heterocyclic compounds [1,2]. Recently the Vilsmeier–Haack reaction has been attracting much attention. For example, the formylation or acylation of arenes, heterocyclic compounds, acetophenone oximes has been recently reported [3–6]. As continuation of our interest in the chemical transformation of perfluoroalkanesulfonylamines $R_fSO_2NH_2$ [7–9], we report the reaction of R_fSO_2NHNa with Vilsmeier reagents.

2. Results and discussion

It is well known that a formylation reaction can be easily achieved by the Vilsmeier–Haack reaction, however, treatment of sodium perfluoroalkanesulfonylamides R_fSO_2NHNa **1** with Vilsmeier reagents $[YCH{=}^+NR_2]Cl^-$ ($Y \equiv OP(O)Cl_2$, $OS(O)Cl$) **2** did not give the expected formylated product R_fSO_2NHCHO. In this reaction the formylated products eliminated hydrogen chloride and gave the corresponding *N*,*N*-dialkyl-*N′*-perfluoroalkanesulfonylformamidine, $R_fSO_2N{=}CHNR_2$, thus:

$$HC(O)NR_2 + YCl \xrightarrow[2\ h]{5\ ^\circ C} [Y{-}CH{=}\underset{\mathbf{2}}{\overset{+}{N}}R_2]Cl^-$$

where $R \equiv CH_3, C_2H_5$; $Y \equiv OS(O)Cl, OP(O)Cl_2$.

$$\mathbf{2} + \underset{\mathbf{1}}{R_fSO_2NHNa} \xrightarrow[\text{r.t., 8 h}]{-\ YONa} [R_fSO_2\overset{+}{N}H{-}CH{=}NR_2]Cl^- \xrightarrow{-\ HCl} R_fSO_2N{=}\underset{\mathbf{3}}{CHNR_2}$$

where $R_f \equiv C_4F_9$, $I(CF_2)_2O(CF_2)_2$, $H(CF_2)_2O(CF_2)_2$.

The yields, boiling or melting points of products **3** are shown in Table 1.

Products **3a**–**3c** are colorless solids and easily recrystallized from many organic solvents such as CH_3CN, CH_3COCH_3, tetrahydrofuran etc.; compounds **3d**–**3f** are high boiling oils. The pure products were obtained by column chromatography or vacuum fractional distillation. It was noticed that compounds **3a**–**3f** are very stable towards acids and bases, they did not hydrolyze under acidic or basic reaction conditions. For example, when **3b** was stirred for 8 h in 36% HCl solution or in 30% NaOH solution, it was almost quantitatively recovered. However, similar compounds such as $R_fSO_2N{=}CHAr$, $R_fSO_2N{=}CHOR$ hydrolyzed to the corresponding $R_fSO_2NH_2$, ArCHO or HCO_2R products when exposed to air. Compound **3a** $C_4F_9SO_2N{=}CHNMe_2$ was first prepared by Niederprum et al. [10] by a two-step reaction from $C_4F_9SO_2F$, thus:

$$C_4F_9SO_2F + (Me_3Si)_2NH \xrightarrow[\text{autoclave}]{200\ ^\circ C} C_4F_9SO_2NHSiMe_3 \xrightarrow{DMF} C_4F_9SO_2N{=}CHNMe_2$$

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Table 1
Compounds **3** prepared

Compounds **3**			Melting point (°C) or boiling point (°C (Torr))	Yield (%)[b]
R	R_f			
Me	C_4F_9	**3a**[a]	72	81
Me	$IC_2F_4OC_2F_4$	**3b**	40	83
Me	$HC_2F_4OC_2F_4$	**3c**	60	80
Et	C_4F_9	**3d**	138–140 (2)	78
Et	$IC_2F_4OC_2F_4$	**3e**	150–152 (2)	75
Et	$HC_2F_4OC_2F_4$	**3f**	140–142 (2)	78

[a]**3a** is a known compound: see Ref. [10].
[b]Isolated yields based on R_fSO_2NHNa.

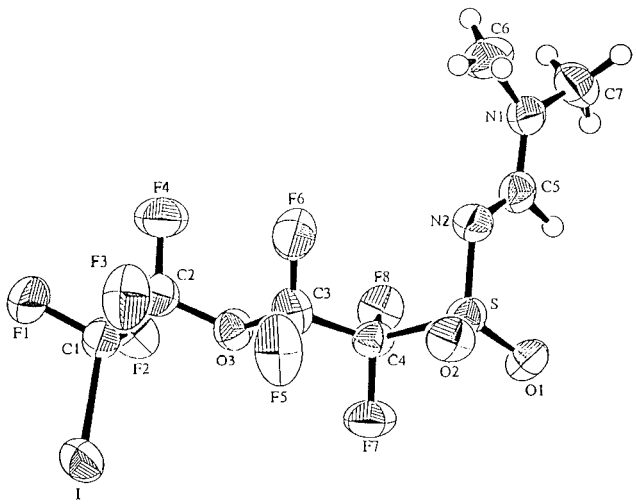

Fig. 1. The molecular structure of **3b**.

The first reaction was carried out in an autoclave at 200 °C and the yield was only 20%. The total yield was 12%.

The stability of compounds **3** could be attributed to electron delocalization.

$$R_fSO_2N'{=}CHNR_2 \longleftrightarrow R_f{-}S(O^{\delta-})(=O){-}N{=}CH{-}NR_2^{\delta+}$$

The X-ray molecular structure analysis of compound **3b** confirmed this point. The bond lengths of N′–C (1.336 Å) and N–C (1.287 Å) are nearly equal (Fig. 1 and Table 2) and both have double bond character.

In conclusion, *N*-perfluoroalkanesulfonylformamidines are conveniently prepared by the Vilsmeier–Haack reaction of perfluoroalkanesulfonylamides R_fSO_2NHNa in good yield. Their chemical properties are now under investigation.

3. Experimental details

Melting and boiling points reported are uncorrected. Solvents were purified and dried before use. ^{1}H NMR (60 MHz) and ^{19}F NMR (54.6 MHz) spectra were recorded on a Varian-360L instrument or Bruker AM-300 spectrometer with TMS and TFA ($\delta_{CFCl_3} = \delta_{TFA} + 76.8$ ppm, and with upfield positive) as an internal and external standard respectively. X-ray structure analysis was performed with a Rigaku/AFC 7R diffractometer. IR spectra were obtained with an IR-440 Shimadzu spectrophotometer. Low resolution mass spectra were obtained on a Finnigan GC-MS 4021 instrument. Elemental analyses were performed by this institute.

3.1. Preparation of compounds *3*

The following general procedure was used for synthesis of compounds **3a**–**3f**. Phosphorus oxychloride (1.6 g, 10.4 mmol) was added to a 25 ml flask containing DMF (5 ml) at 0–5 °C; after addition this solution was stirred for 1 h. $I(CF_2)_2O(CF_2)_2NHNa$ (4.5 g, 10 mmol) was added and then stirred at room temperature (r.t.) for 7 h. The reaction mixture was washed with $NaHCO_3$ solution and water, the oil layer was separated and the aqueous layer was extracted with ether (3×10 ml). The organic layer was combined and dried, after removal of the solvent the crude product was obtained. Recrystallization from CH_3CN gave the fine colorless solid **3b** (3.8 g).

Compounds **3a, 3c, 3d, 3e** and **3f** are prepared similarly.

3.1.1. *$C_4F_9SO_2N{=}CHN(CH_3)_2$* ***3a***

^{1}H NMR ($CDCl_3$) δ (ppm): 8.02 (N=CH, s), 3.15 (CH_3, s), 3.25 (CH_3, s). ^{19}F NMR ($CDCl_3$) δ (ppm): 3.0 (CF_3, s), 35.8 (SO_2CF_2, t), 43.5 (CF_2, s), 48.4 (CF_2, t). IR (ν_{max}, cm^{-1}): 2980 (w), 1650 (s), 1480 (w), 1420 (s), 1340 (s), 1240–1160 (vs), 1030 (m), 1010 (m), 940 (s), 860 (m), 820 (m), 800 (m), 720 (m). MS (*m*/*e* %): 296 (M^+-H-$CHNMe_2$, 2.90), 149 (M^+-SO_2-NCHN-C_2F_4, 32.48), 135 ($^+SO_2N{=}CHMe_2$, 100.00), 71 ($^+N{=}CHNMe_2$, 33.08), 44 (NMe_2^+, 64.59).

3.1.2. *$ICF_2CF_2OCF_2CF_2SO_2N{=}CHN(CH_3)_2$* ***3b***

^{1}H NMR ($CDCl_3$) δ (ppm): 8.10 (N=CH, s), 3.20 (CH_3, s), 3.10 (CH_3, s). ^{19}F NMR ($CDCl_3$): −12.5 (ICF_2, s), 4.0 (OCF_2, t), 8.0 (CF_2O, m), 40.6 (SO_2CF_2, s). IR (ν_{max}, cm^{-1}): 2980 (w), 1630 (s), 1420 (s), 1340 (s), 1220–1100

Table 2
The bond lengths and bond angles of **3b**

Atom	*Atom*	*Distance*	*Atom*	*Atom*	*Distance*
I	C(1)	2.122(6)	S	O(1)	1.436(4)
S	O(2)	1.423(4)	S	N(2)	1.569(4)
S	C(4)	1.851(5)	F(1)	C(1)	1.337(6)
F(2)	C(1)	1.336(7)	F(3)	C(2)	1.336(7)
F(4)	C(2)	1.338(7)	F(5)	C(3)	1.324(7)
F(6)	C(3)	1.318(7)	F(7)	C(4)	1.344(6)
F(8)	C(4)	1.341(6)	O(3)	C(2)	1.375(7)
O(3)	C(3)	1.381(7)	N(1)	C(5)	1.287(7)
N(1)	C(6)	1.453(8)	N(1)	C(7)	1.460(8)
N(2)	C(5)	1.336(8)	C(1)	C(2)	1.519(8)
C(3)	C(4)	1.538(8)			

Atom	*Atom*	*Atom*	*Angle*	*Atom*	*Atom*	*Atom*	*Angle*
O(1)	S	O(2)	117.7(3)	O(1)	S	N(2)	115.2(3)
O(1)	S	C(4)	102.9(2)	O(2)	S	N(2)	109.9(3)
O(2)	S	C(4)	105.0(3)	N(2)	S	C(4)	104.4(2)
C(2)	O(3)	C(3)	121.4(4)	C(5)	N(1)	C(6)	121.7(5)
C(5)	N(1)	C(7)	121.0(5)	C(6)	N(1)	C(7)	117.3(5)
S	N(2)	C(5)	117.6(4)	I	C(1)	F(1)	109.9(4)
I	C(1)	F(2)	109.2(4)	I	C(1)	C(2)	114.7(4)
F(1)	C(1)	F(2)	107.4(5)	F(1)	C(1)	C(2)	107.4(5)
F(2)	C(1)	C(2)	108.0(5)	F(3)	C(2)	F(4)	106.7(5)
F(3)	C(2)	O(3)	111.6(5)	F(3)	C(2)	C(1)	109.7(5)
F(4)	C(2)	O(3)	110.5(5)	F(4)	C(2)	C(1)	109.2(5)
O(3)	C(2)	C(1)	109.1(5)	F(5)	C(3)	F(6)	108.4(5)
F(5)	C(3)	O(3)	110.1(5)	F(5)	C(3)	C(4)	109.3(5)
F(6)	C(3)	O(3)	112.2(5)	F(6)	C(3)	C(4)	110.6(5)
O(3)	C(3)	C(4)	106.1(5)	S	C(4)	F(7)	106.8(3)
S	C(4)	F(8)	107.6(4)	S	C(4)	C(3)	117.7(4)
F(7)	C(4)	F(8)	107.8(4)	F(7)	C(4)	C(3)	107.5(5)
F(8)	C(4)	C(3)	108.9(4)	N(1)	C(5)	N(2)	122.7(5)

(vs), 990 (m), 910 (s), 850 (m), 760 (m), 720 (m), 620 (s). MS (*m*/*e* %): 479 (M^+H, 0.26), 351 (M^+-I, 2.52), 177 (ICF_2^+, 4.12), 135 ($^+SO_2N{=}CHNMe_2$, 100.00), 119 ($C_2F_5^+$, 13.49), 91 ($^+SO_2N{=}CH$, 0.59), 71 ($^+N{=}CHNMe_2$, 13.83), 44 ($^+NMe_2$, 19.14). Element analysis for $C_7H_7F_8N_2O_3SI$: required C 17.57, H 1.46, N 5.58, F 31.80%; found C 17.60, H 1.43, N 5.61, F 31.75%.

3.1.3. $HCF_2CF_2OCF_2CF_2SO_2N{=}CHN(CH_3)_2$ **3c**

^{1}H NMR($CDCl_3$) δ (ppm): 8.13 (N=CH, s), 5.63 (HCF_2, t-t, J_{HF} = 54.0 Hz), 3.23 (CH_3, s), 3.10 (CH_3, s). ^{19}F NMR ($CDCl_3$): 4.1 (OCF_2, s), 8.2 (CF_2O, s), 40.5 (SO_2CF_2, s), 60.3 (HCF_2, d). IR (ν_{max}, cm^{-1}): 3022 (s), 1647 (s), 1437 (s), 1429 (s), 1335 (s), 1285 (s), 1200–1131 (vs), 996 (vs), 860 (s), 752 (s), 698 (s). MS (*m*/*e* %): 353 (M^+H, 15.30), 333 (M^+-F, 1.43), 269 (M^+-F-SO_2, 2.59), 217 ($HC_2F_4OC_2F_4^+$, 13.6), 135 ($^+SO_2N{=}CHNMe_2$, 100.00), 119 ($C_2F_5^+$, 21.62), 101 ($HC_2F_4^+$, 8.20), 71 ($^+N{=}CHNMe_2$, 16.53), 44 ($^+NMe_2$, 32.27). Element analysis for $C_7H_8F_8N_2O_3S$: required C 23.88, H 2.27, N 7.96, F 43.18%; found C 24.35, H 2.23, N 7.92, F 43.41%.

3.1.4. $C_4F_9SO_2N{=}CHN(CH_2CH_3)_2$ **3d**

^{1}H NMR ($CDCl_3$) δ (ppm): 8.02 (N=CH, s), 3.00–3.40 (2×CH_2, m), 1.20–0.8 (2×CH_3, m). ^{19}F NMR ($CDCl_3$) δ (ppm): 5.0 (CF_3, t), 38.5 (SO_2CF_2, t), 45.8 (CF_2, s), 50.0 (CF_2, t). IR (ν_{max}, cm^{-1}): 2980 (m), 1640 (vs), 1440 (s), 1360 (s), 1240–1110 (vs), 1030 (m), 960 (s), 890 (m), 779 (m), 730 (m). MS (*m*/*e* %): 383 (M^+H, 20.56), 339 (M^+H-CH_3-C_2H_5, 5.16), 219 ($C_4F_9^+$, 3.93), 163 ($^+SO_2N{=}CHNEt_2$, 100.00), 99 ($^+N{=}CHNEt_2$, 10.53), 72 ($^+NEt_2$, 46.03). Element analysis for $C_9H_{12}F_9N_2O_2S$: required C 28.20, H 3.13, N 7.31, F 44.65%; found C 28.16, H 2.99, N 7.36, F 44.68%.

3.1.5. $ICF_2CF_2OCF_2CF_2SO_2N{=}CHN(CH_2CH_3)_2$ **3e**

^{1}H NMR ($CDCl_3$) δ (ppm): 8.00 (N==CH, s), 3.45–3.35 (2×CH_2, m), 1.35–1.05 (2×CH_3, m). ^{19}F NMR ($CDCl_3$): −11.5 (ICF_2, s), 4.5 (OCF_2, t), 8.5 (CF_2O, m), 40.0 (SO_2CF_2, s). IR (ν_{max}, cm^{-1}): 2980 (w), 1630 (s), 1420 (s), 1340 (s), 1220–1100 (vs), 990 (m), 910 (s), 850 (m), 760 (m), 720 (m), 620 (s). MS (*m*/*e* %): 507 (M^+H, 2.19), 328 (M^+-H-ICF_2, 2.45), 227 ($IC_2F_4^+$, 31.37), 163 ($^+SO_2N{=}CHNEt_2$, 100.00), 99 ($^+N{=}CHNEt_2$, 8.53), 72 ($^+NEt_2$, 5.26). Element analysis for $C_9H_{11}F_8N_2O_3SI$: required C 21.34, H 1.98, N 5.53, F 30.04%; found C 21.09, H 2.01, N 5.60, F 30.01%.

3.1.6. $HCF_2CF_2OCF_2CF_2SO_2N{=}CHN(CH_2CH_3)_2$ **3f**

^{1}H NMR ($CDCl_3$) δ (ppm): 8.10 (N=CH, s), 6.00 (HCF_2, t-t, J_{HF} = 54.0 Hz), 3.55–3.40 (2×CH_2, m), 1.35–1.15 (2×CH_3, m). ^{19}F NMR ($CDCl_3$) δ (ppm): 3.8 (OCF_2,

m), 9.4 (CF_2O, m), 40.3 (SCF_2, s), 61.0 (HCF_2, d). IR (ν_{max}, cm^{-1}): 2980 (m), 1628 (vs), 1452 (s), 1351 (s), 1340 (vs), 1285–1180 (vs), 997 (s), 963 (s), 895 (s), 861 (m), 797 (s), 774 (s), 752 (s). MS (m/e %): 381 (M^+H, 27.23), 337 (M^+H-CH_3-C_2H_5, 4.17), 163 ($^+SO_2N{=}CHNEt_2$, 100.00), 99 ($^+N{=}CHNEt_2$, 18.99), 72 ($^+NEt_2$, 53.24). Element analysis for $C_9H_{12}F_8N_2O_3S$: required C 28.42, H 3.18, N 7.36%; found C 28.33, H 3.08, N 7.22%.

3.2. Hydrolysis of **3b**

A solution of **3b** (0.48 g, 1 mmol), NaOH (1.5 g), and water (5 ml) was stirred at room temperature for 8 h; ether (10 ml) was added and the ether layer was separated. The aqueous layer was extracted with ether (3×10 ml), the ether layer was combined and the solvent dried; **3b** (0.45 g) was recovered. A similar treatment of **3b** with HCl (36%) was carried out. It was also quantitatively recovered.

3.3. Crystal structure analysis

$C_7H_7O_3F_8N_2IS$: $M=478.10$, monoclinic, space group $C2/c$, $a=20.962(9)$, $b=14.125(3)$, $c=10.717(2)$ Å, $\beta=110.47(2)°$, $V=2972$ Å^3, $Z=8$, $D_c=2.136$ g cm^{-3}. Absorption coefficient 0.324 mm^{-1}, $F(000)=1842$. Radiation, Mo Kα ($\lambda=0.710689$ Å). Crystal dimensions, 0.2×0.2×0.3 mm^3. Intensity data were collected at 20 °C with a Rigaku/AFC 7R diffractometer using graphite-monochromated Mo Kα radiation. A total of 2812 independent reflections was measured in the range $3°<2\theta<50°$ with $0<h<9$, $-13<k<13$, $-14<l<14$. The structure was solved via a direct method using a Siemens system. The positions for all H atoms were obtained by theoretical calculations. All positional parameters and anisotropic thermal parameters for non-H atoms were refined by means of a full-matrix least squares technique. The final R and R_w values were 0.039 and 0.054 respectively, for 2732 observed reflections ($F>4\sigma(F)$). All calculations were performed on a MICRO VAXII computer with SHELX86 and ORTEP programs.

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References

[1] R.M. Acheson, An Introduction to the Chemistry of Heterocyclic Compounds, 3rd edn., Wiley, New York, 1976.
[2] G.A. Olah, L. Ohannesian, M. Arranahaghi, Chem. Rev. 87 (1987) 671.
[3] A. Kawada, S. Mitamura, S. Kobayashi, J. Chem. Soc. Chem. Commun. (1993) 1157.
[4] S.V. Pansara, R.G. Ravi, Synth. Lett. (1994) 823.
[5] R.A. Pawar, P.B. Bajare, S.B. Mundade, J. Indian Chem. Soc. 67 (1990) 685.
[6] I.M. Downie, M.J. Earl, H. Heaney, K.F. Shuhaibar, Tetrahedron 49 (1993) 4015.
[7] S.Z. Zhu, J. Chem. Soc. Chem. Commun. (1991) 732.
[8] S.Z. Zhu, A.W. Li, B. Xu, J. Fluorine Chem. 69 (1994) 257.
[9] S.Z. Zhu, A.W. Li, Y.H. Zhu, J. Fluorine Chem. 60 (1993) 283.
[10] H. Niederprum, P. Voss, V. Beyl, Liebigs. Ann. Chem. 767 (1973) 20.