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Perfluoroalkylation of heterocumulenes with trimethyl(perfluoroalkyl)silanes in the presence of fluoride ions: synthesis of perfluoroalkanesulfinyl amides from *N*-organylsulfinyl amines

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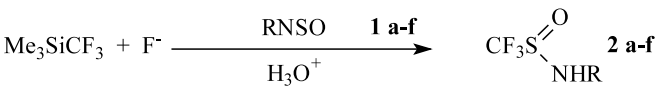
Abstract—Trimethyl(perfluoroalkyl)silanes react in the presence of fluoride ions with *N*-organylsulfinylamines under mild conditions to give the corresponding perfluoroalkanesulfinyl amides in high yields.

Trimethyl(trifluoromethyl)silane, Me_3SiCF_3, in the presence of fluoride ion represents a source of trifluoromethyl nucleophiles which recently enabled the easy and convenient preparations of a variety of trifluoromethyl-containing compounds and to synthesise new fluorinated molecules.[1–3] Its use in heterocumulene transformations, namely isocyanates and isothiocyanates trifluoromethylation to give the corresponding trifluoroacetamides and trifluorothioacetamides, was recently demonstrated.[4]

In extension of our systematic studies on reactions of perfluoroalkyl and pentafluorophenyl anions generated from the corresponding fluor-containing tetraorganosilanes in the presence of fluoride ions with heterocumulenes of the type R–X=Y=Z, with X = N, S; Y = C, S; Z = O, S in different combinations, we now report on the reactions of *N*-alkyl(aryl)sulfinylamines with Me_3SiR_f ($R_f = CF_3$, C_2F_5) in the presence of tetramethylammonium and cesium fluorides.

It must be mentioned that nucleophilic addition of organometallic compounds (magnesium and lithium) to –N=S=O bonds was investigated comprehensively[5] whereas, to the best of our knowledge, the interaction of perfluoroalkylating reagents with this functional group has not yet been investigated.

Perfluoroalkanesulfinyl amides are rarely documented in literature; few compounds (mainly trifluoromethanesulfinyl amides) were obtained from reactions of amines with corresponding sulfinyl chlorides.[6] The latter are difficult to obtain and, if commercially available, are very expensive and therefore less suitable as starting materials. Recently, solutions of sodium trifluoromethanesulfinate and phosphoryl chloride were



a = t-Bu, **b** = PhCHMe, **c** = c-C_6H_{11}, **d** = Ph, **e** = 3-F-C_6H_4, **f** = 3-CF_3-C_6H_4

Scheme 1.

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used to prepare trifluoromethanesulfinyl amides from amines.[7]

We found that reactions of *N*-alkyl(aryl)sulfinyl amines **1a–f** with Me_3SiCF_3 in the presence of tetramethylammonium fluoride in THF or monoglyme at −60 to −50°C, followed by protolysis with aqueous ammonium chloride, give the corresponding *N*-substituted trifluoromethanesulfinyl amides **2a–f** in 75–85% yield (Scheme 1).[7]

Reaction intermediates in all cases are tetramethylammonium salts of the *N*-substituted trifluoromethanesulfinyl amides which are directly formed as colourless precipitates after mixing of the reagents. These salts appear to be unstable but we succeeded in the isolation and characterisation of the *N*-*t*-butyl substituted salt **3a** (Scheme 2).[9]

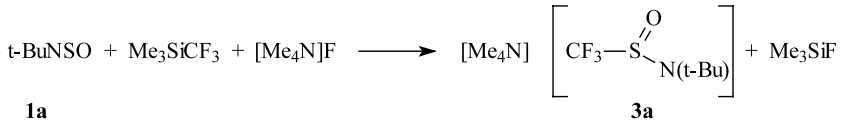
The intermediate formation of salts such as **3a** opens an easy and convenient route to one-pot syntheses of *N*,*N*-disubstituted trifluoromethanesulfinyl amides. Methylation of the salt formed from phenylsulfinyl amine with iodomethane gave *N*-phenyl-*N*-methyltrifluoromethanesulfinyl amide in 87% yield (Scheme 3). Spectroscopic and analytical data are in good agreement with reported ones.[7]

In order to extend these reactions to derivatives of higher perfluoroalkanesulfinic acids, we investigated the principal possibility to synthesise so far unknown amides of pentafluoroethanesulfinic acid. We found that *N*-phenylsulfinyl amine **1d** reacts with trimethyl(pentafluoroethyl)silane in the presence of tetramethylammonium fluoride under above mentioned conditions to form *N*-phenylpentafluoroethanesulfinyl amide **5d** in 80% yield (Scheme 4).[10]

Besides tetramethylammonium fluoride, dry cesium fluoride can also be used as a fluoride source in these reactions that are best performed in propionitrile. In contrast to ethers, temperature of the reaction mixture had to be held at approximately −5°C for 6 hours as demonstrated in the conversion of **1d** into *N*-phenyltrifluoromethylsulfinyl amide **2d** (80% yield).

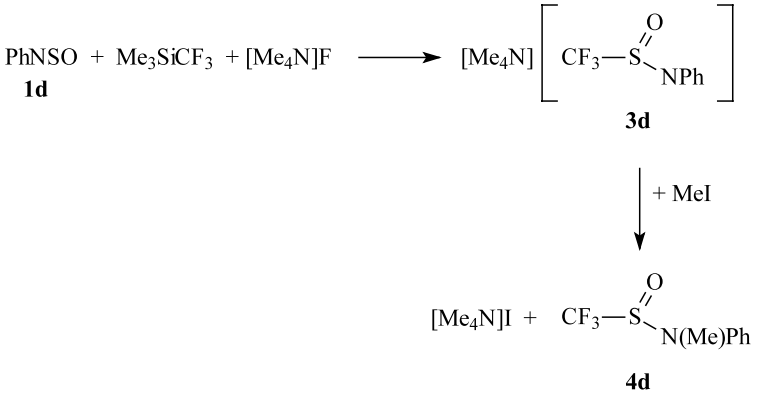
Reaction conditions, yields and physical data of **2a–f** are summarised in Table 1. Analytic data of new or so far not fully characterised compounds are given in Ref. 8.

In summary, a concise and convenient method for the synthesis of perfluoroalkanesulfinyl amides has been developed starting from easily available substances such as sulfinylamines via direct trifluoromethylation using Me_3SiR_f ($R_f = CF_3$, C_2F_5) in the presence of fluoride sources.



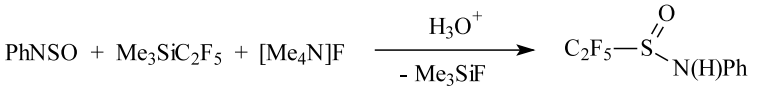
1a **3a**

Scheme 2.



1d **3d** **4d**

Scheme 3.



1d **5d**

Scheme 4.

Table 1. Reactions of *N*-alkyl- and *N*-arylsulfinyl amines with Me_3SiCF_3 and $[Me_4N]F$ in glyme or THF

	R	Reagents (mmol)			Solvent (mL)	Mop[a]	Yield (%)	Mp (°C), bp (°C/Torr)
		RNSO	$[Me_4N]F$	Me_3SiCF_3				
2a	*t*-Bu	2.60	2.60	2.86	5	v.d.	85	85/10
2b	PhCHMe	1.79	1.79	1.97	5	s.	78	56 (oil[7])
2c	c-C_6H_{11}	2.92	2.92	3.21	4	v.d.	75	51–52/0.03
2d	Ph	2.57	2.57	2.83	5	s.	85	64 (64[7])
2e	3-FC_6H_4	2.67	2.67	2.94	4	s.	75	55
2f	3-$CF_3C_6H_4$	3.18	3.18	3.50	6	s.	80	72

[a] Mop: method of purification; vacuum distillation (v.d.), sublimation (s.).

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References

1. Singh, R. P.; Shreeve, J. M. *Tetrahedron* **2000**, *56*, 7613–7632.
2. Prakash, G. K. S.; Yudin, A. K. *Chem. Rev.* **1997**, *97*, 757–786.
3. (a) Furin, G. G. *Zh. Org. Chem.* **1997**, *33*, 1287–1319; (b) Furin, G. G. *Russ. J. Org. Chem.* **1997**, *33*, 1209–1242.
4. Kirij, N. V.; Yagupolskii, Yu. L.; Petukh, N. V.; Tyrra, W.; Naumann, D. *Tetrahedron Lett.* **2001**, *42*, 8181–8183.
5. Krauthausen, E. In *Houben-Weyl Methoden der organischen Chemie; Band E – 11/ Teil 1*; Thieme: Stuttgart, 1985; pp. 658–659.
6. Roesky, H. W.; Tutkunkardes, S. *Chem. Ber.* **1974**, *107*, 508–517.
7. Billard, T.; Greiner, A.; Langlois, B. R. *Tetrahedron* **1999**, *55*, 7243–7250.
8. *General procedure:* To a solution of the appropriate *N*-organylsulfinyl amine in monoglyme (or THF) at −60°C, tetramethylammonium fluoride and trimethyl(trifluoromethyl)silane were added. The mixture was stirred for 2 h at −50°C and for 1 h at room temperature. A 10% aqueous solution of NH_4Cl was added and the product was extracted with diethyl ether. The extract was washed with water, dried ($MgSO_4$), and purified by vacuum distillation or sublimation.
   All compounds were characterised on the basis of analytical and spectroscopic data. Selected data: **2a**: ^{1}H NMR (299.95 MHz, CD_3CN): δ 1.35 (s, 9H, –*t*-Bu), 5.48 (broad s, 1H, –NH); ^{19}F NMR (282.4 MHz, diethyl ether): δ −79.8 (s, 3F). Anal. calcd for $C_5H_{10}F_3NOS$: C, 31.74; H, 5.33; N, 7.40; F, 30.13. Found: C, 32.01; H, 5.65; N, 7.62; F, 30.27. **2c**: ^{1}H NMR (299.95 MHz, CD_3CN): δ 1.35 (s, 9H, –*t*-Bu), 5.48 (broad s, 1H, –NH); ^{19}F NMR (282.4 MHz, CD_3CN): δ −78.1 (s, 3F). Anal. calcd for $C_7H_{12}F_3NOS$: C, 39.06; H, 5.62; N, 6.51; F, 26.48. Found: C, 39.15; H, 5.60; N, 6.72; F, 26.41. **2e**: ^{1}H NMR (299.95 MHz, $CDCl_3$): δ 6.74–6.83 (m, 3H, –Ar and 1H, –NH), 7.19–7.28 (m, 1H, –Ar); ^{19}F NMR (282.4 MHz, $CDCl_3$): δ −78.3 (s, 3F), −110.8 (broad s, 1F). Anal. calcd for $C_7H_5F_4NOS$: C, 37.01; H, 2.22; N, 6.17; F, 33.45. Found: C, 37.34; H, 2.09; N, 6.41; F, 33.67. **2f**: ^{1}H NMR (299.95 MHz, $CDCl_3$): δ 6.75 (broad s, 1H, –NH), 7.27–7.34 (m, 2H, –Ar), 7.42–7.52 (m, 2H, –Ar); ^{19}F NMR (282.4 MHz, CD_3CN): δ −62.6 (s, 3F, –$CF_3C_6H_4$), −77.0 (s, 3F). Anal. calcd for $C_8H_5F_6NOS$: C, 34.66; H, 1.82; N, 5.05; F, 41.13. Found: C, 34.80; H, 1.98; N, 5.16; F, 41.32.
9. **3a**: To a solution of 3.1 mmol *N*-*t*-butylsulfinylamine in 7 mL THF at −80°C, 3.1 mmol tetramethylammonium fluoride and 3.41 mmol trimethyl(trifluoromethyl)silane were added. The mixtures was stirred for 2 h at −45°C and for 1 h at room temperature. The solvent was evaporated, the residue was dried in vacuum. Yield 93%, mp 65°C (decomp). ^{1}H NMR (299.95 MHz, DMSO-d_6): δ 1.04 (s, 9H, –*t*-Bu), 3.10 (s, 12H, Me_4N); ^{19}F NMR (282.4 MHz, DMSO-d_6): δ −80.46 (s, 3F). Anal. calcd for $C_9H_{21}F_3N_2OS$: C, 41.20; H, 8.07; N, 10.68; F, 21.73; S, 12.22. Found: C, 41.37; H, 8.30; N, 10.55; F, 21.87; S, 12.16.
10. **5d**: To a solution of 2.54 mmol *N*-phenylsulfinylamine in 5 mL THF at −80°C, 2.54 mmol tetramethylammonium fluoride and 2.79 mmol trimethyl(pentafluoroethyl)silane were added. The mixture was stirred for 2 h at −60°C. A 10% aqueous solution of NH_4Cl was added at −30°C and the product was extracted with diethyl ether. The extract was washed with water, dried ($MgSO_4$), and purified by sublimation. Yield 80%, mp 38°C. ^{1}H NMR (299.95 MHz, $CDCl_3$): δ 7.07 (m, 2H), δ 7.18 (m, 1H), 7.34 (m, 2H), 6.50 (broad s, 1H, –NH); ^{19}F NMR (282.4 MHz, $CDCl_3$): δ −79.8 (s, 3F), −121.5 and −125 (AB system, $^2J_{FF}$ = 245.4 Hz). Anal. calcd for $C_8H_6F_5NOS$: C, 37.07; H, 2.33; N, 5.40; F, 36.65. Found: C, 36.89; H, 2.15; N, 5.26; F, 36.77.