Condensation Reaction of *N*-Sulphinylperfluoroalkanesulphonamides

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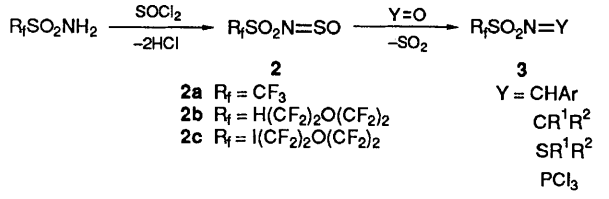
N-Sulphinylperfluoroalkanesulphonamides, R_fSO_2NSO, which are prepared by refluxing of perfluoroalkanesulphonamides with thionyl chloride, react easily with aldehydes, ketones, sulphoxides and phosphorus trichloride oxide yielding a series of new compounds $R_fSO_2N{=}Y$ (Y = CHAr, CR^1R^2, SR^1R^2 and PCl_3) with elimination of sulphur dioxide.

Although *N*-sulphinyltrifluoromethanesulphonamide, CF_3SO_2NSO, was first prepared twenty years ago,[1] its chemistry has not been thoroughly studied yet. The only report was its reactions with fluorine[2] and benzenaldehyde.[3] In connection with our interest in the chemistry of perfluoroalkanesulphonamides and derivatives, it was found that R_fSO_2NSO **2** are very reactive. The strong electron-withdrawing property of the $R_fSO_2N{=}$ group[3,4] makes the sulphinyl sulphur of **2** very electrophilic. By analogy with CF_3SO_2NCO,[5] **2** would be expected to react with a range of nucleophiles (NuH), such as

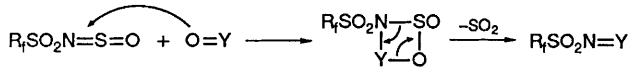
Table 1

Entry	2	Y=O	Reaction conditions T/°C	Reaction conditions t/h	Product 3	Yield (%)[a]	B.p./°C at 1 mmHg
1	**2a**	PhCHO	80[b]	12	**3a**	58	86–88[c]
2	**2b**	PhCHO	80[b]	12	**3b**	62	105–107
3	**2b**	$CH_2[CH_2]_4C=O$	100	12	**3c**	55	92–94
4	**2b**	$CH_2[CH_2]_3S=O$	r.t.[b]	0.5	**3d**	72	122–124
5	**2b**	$Cl_3P=O$	r.t.	8	**3e**	65	80–83
6	**2c**	$Me_2S=O$	r.t.[b]	0.5	**3f**	78	122
7	**2c**	$Cl_3P=O$	r.t.	8	**3g**	61	85–87

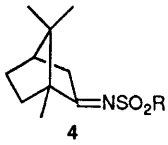
[a] Isolated yield. [b] Reaction in CCl_4. [c] M.p. 31–32 °C. r.t. = room temperature.



Scheme 1



Scheme 2



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ROH, RNH_2 and ArOH giving $R_fSO_2NHSONu$.[6] When **2** was treated with other kinds of reagents, *e.g.* ArCHO, cyclohexanone, $R_2S=O$ and $Cl_3P=O$, sulphur dioxide was evolved forming the substituted imines $R_fSO_2N=Y$ (Y = CHAr, CR^1R^2, SR^1R^2 and PCl_3), see Scheme 1.†

It is possible that a four-membered ring intermediate may be involved in the reaction (Scheme 2).

The reactions of **2** with aldehydes and ketones occurred at 80–100 °C, whereas SO_2 was evolved immediately when the more polar sulphoxides and phosphine oxide were mixed with **2** at room temperature.

All the products **3** were moisture-sensitive, *e.g.* $R_fSO_2N=CHPh$ **3b** decomposed to $R_fSO_2NH_2$ and PhCHO during purification using column chromatography. The pure products were obtained only by several vacuum distillations. This contrasts with the behaviour of the camphor derivative **4**, containing a non-fluoro substituent, which required refluxing in HCl solution[7] for hydrolysis to the sulphonamide. The large difference could be ascribed to the greater electronegativity of the R_fSO_2 group.

All new compounds give satisfactory elemental analyses and the IR, ^1H NMR, ^{19}F NMR and mass spectra are consistent with the shown structures.‡

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† Compounds **2** were prepared by literature methods.[1] Equimolar quantities of **2** and Y=O were stirred under reflux until the evolution of SO_2 stopped; the mixture was then distilled *in vacuo*. After several distillations, pure products **3** were obtained.

‡ *Spectral data* for: **2b**, $HCF_2CF_2OCF_2CF_2SO_2NSO$, b.p. 56–58 °C at 1 mmHg; ^1H NMR ($SiMe_4$), δ 6.05 (t, 1H, $^2J_{HF}$ 55 Hz). ^{19}F NMR (CF_3CO_2H) δ 62.1 d, $^2J_{HF}$ 55 Hz, HCF_2), 5.1 (m, CF_2O) 12.5 (m, OCF_2), 40.7 (s, CF_2SO_2). IR ν/cm^{-1} (KCl), 2923w, 1423w, 1390s, 1287s, 1202vs, 1125s, 1100s, 980s, 928m, 612m, 550m. Mass spectrometry (*m/z*): 344 (M^+ + 1, 4.84), 343 (M^+, 28.87), 278 (M^+ − H−SO_2, 16.68), 226 (M^+ − $H(CF_2)_2O$, 3.48), 180 ($^+OCF_2CF_2SO_2$, 25.34), 162 ($^+CF_2CF_2SON$, 11.92), 101 [$H(CF_2)_2^+$, 12.38], 110 (SO_2NS^+, 36.44), 100 ($^+CF_2CF_2$, 22.91), 80 (SOS^+, 14.71), 65 ($^+SO_2H$ or HCF_2N^+, 100). **3b**, $HCF_2CF_2OCF_2CF_2SO_2N=CHPh$, ^1H NMR, δ 8.50 (s, =CH), 7.30 (m, 2H), 6.97 (m, 3H), 5.35 (t, 1H, $^2J_{HF}$ 55 Hz). ^{19}F NMR, δ 62.1 (d, HCF_2), 5.0 (t, CF_2O), 12.6 (m, OCF_2), 41.0 (s, CF_2SO_2). IR ν/cm^{-1}, 3030m, 1624m, 1590m, 1380vs, 1328s, 1290s, 1200vs, 1128s, 982s, 930m, 855m, 610m. Mass spectrometry (*m/z*): 386 (M^+ + 1, 41.60), 366 (M^+ −F, 1.46), 302 (M^+ −F−SO_2, 2.49), 168 [M^+ −$H(CF_2)_2O(CF_2)_2$, 7.64], 154 ($PhCH{=}SO_2^+$, 12.64), 152 ($PhCH{=}NSO^+$, 17.8), 104 ($PhCH{=}N^+$, 75.19), 101 ($HCF_2CF_2^+$, 25.39), 77 (Ph^+, 100), 64 (SO_2^+, 4.77), 51 (HCF_2^+, 34.70).