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Synthesis and cycloaddition reactions of polyfluorinated imines

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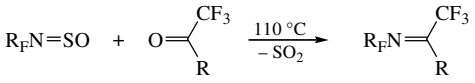
Imines 3–6 containing fluorinated N-substituents were prepared by reactions of fluorinated sulfinylamines 1, 2 with hexafluoroacetone and ethyl trifluoropyruvate; trifluoromethylsulfonylimines 3, 5 exothermically reacted with dienes at –50 °C to form cycloaddition products 7, 9 and α-aminoalkylation products 8, 10.

Polyfluorinated imines are precursors for the preparation of fluorinated nitrogen-containing heterocyclic compounds by cycloaddition reactions.[1,2] However, methods for the synthesis of imines with fluorinated N-substituents have been inadequately developed and some of these compounds are preparatively unavailable.[2,3] In particular, highly electrophilic N-perfluoroalkylsulfonylimines of fluorinated ketones were obtained only by the deoxygenation of corresponding oxaziridines.[4]

The aim of this study was to prepare imines with fluorinated N-substituents. As parent compounds, we used available trifluoromethylsulfonylsulfinylamine[5] **1** and pentafluorophenylsulfinylamine[6] **2** because non-fluorinated sulfinylamines were successfully used previously for the synthesis of hexafluoroacetone arylimines[7] and 2-iminotrifluoropropionates.[8] We believed that the enhanced electrophilicity of these reagents will hinder reactions with polyfluorinated carbonyl compounds. We found that the reactions of compounds **1**, **2** with ethyl trifluoropyruvate occurred at 110 °C with the elimination of SO_2 and the formation of imines **3**, **4** in 35 and 61% yields, respectively. Analogous reactions with hexafluoroacetone did not occur even at higher temperatures (to 200 °C). Imines **5**, **6** were prepared in 69 and 11% yields, respectively, at 110 °C only under conditions of CsF catalysis (Scheme 1).† In the latter case, the conversion of reagents did not increase with temperature (≈150 °C); this fact is indicative of an equilibrium character of this process.

The reactions of sulfinylamines **1**, **2** with trifluoroacetyl chloride did not result in the formation of corresponding imidoyl halides (Scheme 2) even with the use of CsF as a catalyst at high temperatures.

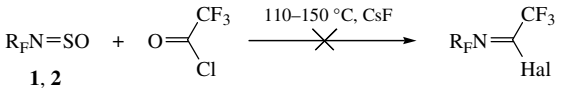
Trifluoropyruvate *N*-trifluoromethylsulfonimine **3** is an extremely electrophilic compound, which emits smoke in air and exothermically reacts with donor dienes even at –40 °C.



1, **2** — **3** $R_F = CF_3SO_2$, R = C(O)OEt; **4** $R_F = C_6F_5$, R = C(O)OEt; **5** $R_F = CF_3SO_2$, $R = CF_3$; **6** $R_F = C_6F_5$, $R = CF_3$

Scheme 1

However, these reactions gave ambiguous results. Imine **5** also exoterically reacts with dienes at –50 °C.‡ The reaction of compound **5** with cyclopentadiene occurred unambiguously with the



1, **2**

Scheme 2

† The ^{1}H and ^{19}F NMR spectra were measured on a Bruker DRX-500 with operating frequencies of 500.1 and 470.6 MHz, respectively. The chemical shifts (δ/ppm) were measured using TMS (^{1}H) and $CFCl_3$ (^{19}F) as external standards. The mass spectra were measured on an HP 5890 II Series gas chromatograph with an HP 5972A MSD mass selective detector. Commercial reagents and solvents were prepared in accordance with well-known procedures.[9]

Synthesis of polyfluorinated ketone imines **3**–**6** *(general procedure).* The mixture of a corresponding sulfinylamine (15.0 mmol) and ethyl trifluoropyruvate (2.3 g, 15.5 mmol) for imines **3**, **4** or hexafluoroacetone (4.9 g, 29.5 mmol) and CsF (0.2 g) for imines **5**, **6** was heated (*a*) (compounds **3**, **4**) for 13 h at 110 °C and cooled to 20 °C; the reaction mixture was fractionated in a vacuum or (*b*) (compounds **5**, **6**) for 20 h at 110 °C in a sealed glass ampule and cooled to –78 °C; volatile components were removed on heating to 20 °C, and the residue was fractionated.

For **3**: yield, 35%; bp 38–39 °C (15 Torr); n_D^{20} 1.3763. ^{1}H NMR, δ: 1.45 (t, 3H, Me, *J* 7.0 Hz), 4.51 (q, 2H, CH_2, *J* 7.0 Hz). ^{19}F NMR, δ: –69.73 (br. s, 3F, CF_3), –77.02 (s, 3F, CF_3SO_2). Found (%): C, 24.17; H, 1.88; N, 4.87. Calc. for $C_6H_5F_6NO_4S$ (%): C, 23.92; H, 1.66; N, 4.65.

For **4**: yield, 61%; bp 79–81 °C (13 Torr); n_D^{20} 1.4189. ^{1}H NMR, δ: 1.37 (t, 3H, Me, *J* 7.0 Hz), 4.42 (q, 2H, CH_2, *J* 7.0 Hz). ^{19}F NMR, δ: –69.72 (s, 3F, CF_3), –149.75 (d, 2F, C_6F_5, *J* 21.0 Hz), –156.84 (t, 1F, C_6F_5, *J* 21.0 Hz), –161.85 (t, 2F, C_6F_5, *J* 21.0 Hz). Found (%): C, 39.94; H, 1.63; N, 4.37. Calc. for $C_{11}H_5F_8NO_2$ (%): C, 39.40; H, 1.49; N, 4.18. MS, *m*/*z* (%): 335 $[M]^+$ (52), 262 (100), 193 (12), 69 (48).

For **5** (data for compound **5** are consistent with previously reported data[4]): yield, 69%; bp 72–73 °C. n_D^{20} 1.3091. ^{19}F NMR, δ: –67.79 (br. s, 6F, CF_3), –77.06 (s, 3F, CF_3SO_2). Found (%): C, 16.37; N, 4.82. Calc. for $C_4F_9NO_2S$ (%): C, 16.16; N, 4.71.

For **6**: yield 11%; bp 32–33 °C (11 Torr). n_D^{20} 1.3789. ^{19}F NMR, δ: –67.86 (s, 3F, CF_3), –70.00 (s, 3F, CF_3), –150.53 (d, 2F, C_6F_5, *J* 21.0 Hz), –156.98 (t, 1F, C_6F_5, *J* 21.0 Hz), –161.56 (t, 2F, C_6F_5, *J* 21.0 Hz). Found (%): C, 32.75; N, 4.37. Calc. for $C_9F_{11}N$ (%): C, 32.62; N, 4.23.

‡ *Reactions of imine* **5** *with dienes (general procedure).* Imine **5** (0.8 g, 2.7 mmol) was added to a solution (5.0 mmol) of a corresponding diene in 5 ml of dry diethyl ether at –50 °C with stirring; next, the mixture was slowly warmed to room temperature. The residue was fractionated in a vacuum for compounds **7**–**12**.

For **7**: yield, 69%; bp 100 °C (10 Torr); n_D^{20} 1.3948. ^{1}H NMR, δ: 1.68 and 3.01 (2H, CH_2, AB-spectrum, J_{AB} –9.0 Hz), 4.72 (s, 1H, CH), 4.89 (s, 1H, CH), 6.51 (br. s, 1H, CH), 6.82 (br. s, 1H, CH). ^{19}F NMR, δ: –60.44 (br. s, 3F, CF_3), –69.38 (br. s, 3F, CF_3), –76.37 (q, 3F, CF_3SO_2, *J* 6.0 Hz). Found (%): C, 29.91; H, 1.81; N, 3.94. Calc. for $C_9H_6F_9NO_2S$ (%): C, 29.75; H, 1.65; N, 3.85.

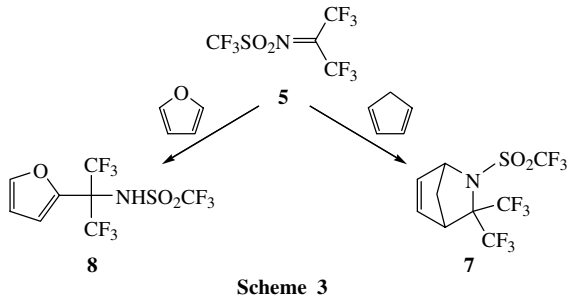
For **8**: yield, 41%; bp 88 °C (12 Torr); n_D^{20} 1.3801. ^{1}H NMR, δ: 6.01 (br. s, 1H, NH), 6.51 (s, 1H, CH), 6.85 (s, 1H, CH), 7.60 (s, 1H, CH). ^{19}F NMR, δ: –72.21 (m, 6F, CF_3), –75.76 (m, 3F, CF_3SO_2). Found (%): C, 26.49; H, 1.18; N, 3.99. Calc. for $C_8H_4F_9NO_3S$ (%): C, 26.30; H, 1.09; N, 3.83.

Mixture of **9** + **10**, bp 58 °C (1 Torr).

For **9**: ^{1}H NMR, δ: 1.83 (br. s, 6H, Me), 2.78 (br. s, 2H, CH_2), 3.59 (br. s, 2H, CH_2). ^{19}F NMR, δ: –66.08 (k, 3F, CF_3, *J* 9.0 Hz), –66.80 (k, 3F, CF_3, *J* 9.0 Hz), –76.45 (m, 3F, CF_3SO_2).

For **10**: ^{1}H NMR, δ: 2.01 (s, 3H, Me), 3.23 (br. s, 2H, CH_2), 5.14 (s, 1H, CH_2), 5.19 (s, 1H, CH_2), 5.32 (s, 1H, CH_2), 5.53 (s, 1H, CH_2), 5.89 (br. s, 1H, NH). ^{19}F NMR, δ: –70.22 (m, 6F, CF_3), –74.23 (m, 3F, CF_3SO_2).

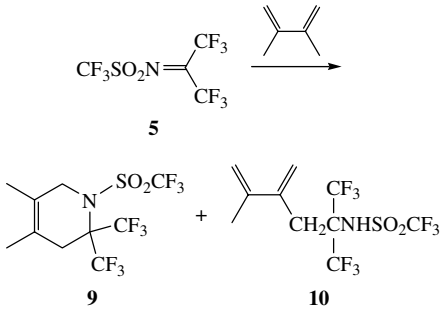
For **11**: MS, *m*/*z* (%): 369 $[M]^+$ (26), 324 (5), 300 (83), 69 (100).



Scheme 3

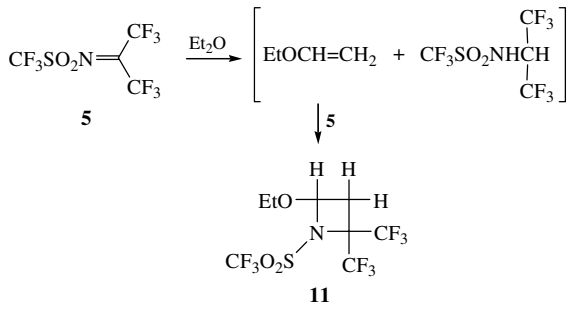
formation of [4+2]-cycloaddition product, azabicycloheptene **7**, in 69% yield. In contrast, the interaction of compound **5** with furan resulted in the release of only α-sulfoimidoalkylation product **8** (Scheme 3).

It is of interest that the reaction of compound **5** with 2,3-dimethylbutadiene occurred ambiguously with the simultaneous formation of both cycloaddition product **9** and ene synthesis product **10** (Scheme 4).



Scheme 4

The reaction with norbornadiene gave a complex mixture of products even at –40 °C. Compound **11** was identified by chromato-mass spectrometry. This compound can result from the oxidative dehydrogenation of diethyl ether (in which the reaction was performed) followed by the [2+2]-cycloaddition of vinyl ethyl ether (Scheme 5).



Scheme 5

Thus, the method developed for the synthesis of imines with fluorinated substituents at the nitrogen atom considerably improves the availability of these compounds. Trifluoromethylsulfonylimines **3**, **5** exhibit extraordinary electrophilicity, which manifests itself in reactions with dienes and diethyl ether. This was supported by extremely low LUMO and HOMO energies of imines **3** (–0.067 and –12.446 eV) and **5** (0.140 and –13.184 eV) *ab initio* calculated using the 3–21G basis set.

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