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#### LETTERS TO THE EDITOR

## **Reaction of Perfluorinated Vinyl Ethers with Diethylamine**

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It is known that perfluorovinyl ethers react with secondary amines to give the corresponding addition products [1]. We have found that trifluoromethyl and heptafluoropropyl trifluorovinyl ethers **Ia** and **Ib** react with diethylamine to give analogous addition products **IIa** and **IIb**.

$$\begin{array}{c} R_FOCF=CF_2+HNEt_2 \rightarrow R_FOCFHCF_2NEt_2, \\ \textbf{Ia, Ib} & \textbf{IIa, IIb} \end{array}$$

 $R_{F} = C_{3}F_{7}(\mathbf{a}), CF_{3}(\mathbf{b}).$ 

In the <sup>19</sup>F NMR spectra of *N*,*N*-diethyl-1,1,2-trifluoro-2-(perfluoroalkoxy)ethanamines **IIa** and **IIb** thus obtained signals from fluorine atoms in the difluoromethylene group appeared as an *AB* spin system, in keeping with the data of [1]. Amines **IIa** and **IIb** turned out to be relatively unstable, and they became yellowish even on storage in a sealed ampule. Treatment of amines **IIa** and **IIb** with water in the presence of triethylamine afforded the corresponding *N*,*N*-diethyl-2-fluoro-2-(perfluoroalkoxy)acetamides **IIIa** and **IIIb**.

$$\begin{array}{c} R_FOCFHCF_2NEt_2 + H_2O + 2 NEt_3\\ \textbf{IIa, IIb} \end{array}$$

# $\rightarrow R_F OCFHC(O)NEt_2 + 2 HF \cdot NEt_3.$ IIIa, IIIb

Amine **IIb** reacted with aniline to produce *N*,*N*-diethyl-2-fluoro-2-trifluoromethoxy-1-(phenylimino)-ethanamine (**IVb**).

$$\begin{array}{c} R_FOCFHCF_2NEt_2+C_6H_5NH_2+2\,NEt_3\\ \textbf{IIb} \end{array}$$

$$\rightarrow R_FOCFHC(=NC_6H_5)NEt_2 + 2 HF \cdot NEt_3.$$
**IVb**

The products structure was confirmed by their <sup>1</sup>H and <sup>19</sup>F NMR spectra.

*N*,*N*-Diethyl-1,1,2-trifluoro-2-heptafluoropropoxyethanamine (IIa) was obtained from 10.5 g of diethylamine and 37.7 g of 1,1,2-trifluoro-2-heptafluoropropoxyethene (Ib) under stirring at 20–25°C. Yield 84%, bp 55–56°C (25 mm). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 5.94 d (1H, CHF, *J*<sub>HF</sub> = 54 Hz), 2.93 q (4H, NCH-<sub>2</sub>, *J*<sub>HH</sub> = 7 Hz), 1.05 t (6H, CH<sub>2</sub>CH<sub>3</sub>, *J*<sub>HH</sub> = 7 Hz). <sup>19</sup>F NMR spectrum,  $\delta_F$ , ppm: -81.7 s (3F, CF<sub>3</sub>), -84.9 d and -87.5 d (1F each, OCF<sub>2</sub>, *J*<sub>FF</sub> = 153 Hz), -87.8 d and -90.7 d (1F each, NCF<sub>2</sub>, *J*<sub>FF</sub> = 206 Hz), -130.0 s (2F, CF<sub>3</sub>CF<sub>2</sub>), -140.5 d (1F, CHF, *J*<sub>FH</sub> = 57 Hz).

*N*,*N*-Diethyl-1,1,2-trifluoro-2-trifluoromethoxyethanamine (IIb) was synthesized in a similar way from diethylamine and 1,1,2-trifluoro-2-trifluoromethoxyethene (Ia). Yield 72%, bp 48–50°C (50 mm). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 5.79 d (1H, CHF, *J*<sub>HF</sub> = 55 Hz), 2.92 q (4H, NCH<sub>2</sub>, *J*<sub>HH</sub> = 7 Hz), 1.05 t (6H, CH<sub>2</sub>CH<sub>3</sub>, *J*<sub>HH</sub> = 7 Hz). <sup>19</sup>F NMR spectrum,  $\delta_F$ , ppm: –59.9 s (3F, CF<sub>3</sub>), –87.8 d and –90.8 d (1F each, CF<sub>2</sub>, *J*<sub>FF</sub> = 205 Hz), –141.5 d (1F, CHF, *J*<sub>FH</sub> = 57 Hz).

*N*,*N*-Diethyl-2-fluoro-2-heptafluoropropoxyacetamide (IIIa) was synthesized by treatment of amine IIa with water in the presence of triethylamine. <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 6.20 d (1H, CHF,  $J_{HF} = 55$  Hz), 3.29 q (4H, NCH<sub>2</sub>,  $J_{HH} = 7$  Hz), 1.10 t (6H, CH<sub>2</sub>CH<sub>3</sub>,  $J_{HH} = 7$  Hz). <sup>19</sup>F NMR spectrum,  $\delta_F$ , ppm: -81.3 s (3F, CF<sub>3</sub>), -84.9 d and -87.2 d (2F, OCF<sub>2</sub>,  $J_{FF} = 147$  Hz), -129.7 s (2F,  $CF_2CF_3$ ), -129.1 d (1F, CHF,  $J_{FH} = 50$  Hz).

*N*,*N*-Diethyl-2-fluoro-2-trifluoromethoxyacetamide (IIIb) was synthesized in a similar way from amine IIb. <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 5.98 d (1H, CHF,  $J_{\text{HF}} = 57$  Hz), 3.14 q (4H, NCH<sub>2</sub>,  $J_{\text{HH}} = 7$  Hz), 0.92 t (6H, CH<sub>2</sub>CH<sub>3</sub>,  $J_{\text{HH}} = 7$  Hz). <sup>19</sup>F NMR spectrum,  $\delta_{\text{F}}$ , ppm: -59.3 s (3F, CF<sub>3</sub>), -131.1 d (1F, CHF,  $J_{\text{FH}} =$ 57 Hz). *N*,*N*-Diethyl-2-fluoro-2-trifluoromethoxy-1-phenyliminoethanamine (IVb). Amine IIa, 8.6 g, was added to a solution of 3.3 g of aniline and 7.7 g of triethylamine in 10 ml of petroleum ether. The mixture was stirred for 3 h at 40–50°C and cooled to room temperature, the precipitate was filtered off, and the filtrate was subjected to vacuum distillation. Yield 9.0 g (61.6%), bp 108–109°C (12 mm). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 7.13 t (2H, *o*-H, *J*<sub>HH</sub> = 8 Hz), 6.87 t (1H, *p*-H, *J*<sub>HH</sub> = 8 Hz), 6.60 d (2H, *m*-H, *J*<sub>HH</sub> = 8 Hz), 6.28 d (1H, CHF,  $J_{\text{HF}} = 52$  Hz), 3.36 q (4H, NCH<sub>2</sub>,  $J_{\text{HH}} = 7$  Hz), 1.10 t (6H, CH<sub>2</sub>CH<sub>3</sub>,  $J_{\text{HH}} = 7$  Hz). <sup>19</sup>F NMR spectrum,  $\delta_{\text{F}}$ , ppm: -58.6 s (3F, CF<sub>3</sub>), -128.4 d (1F, CHF,  $J_{\text{FH}} =$ 57 Hz). Found, %: C 53.08; H 5.28; N 10.23. C<sub>13</sub>H<sub>16</sub>F<sub>4</sub>N<sub>2</sub>O. Calculated, %: C 53.42; H 5.57; N 9.58.

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