Synthesis of new polyfluorinated aza-1,3-dienes

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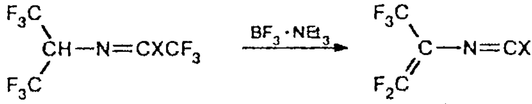
Despite the variety of known ways of synthesis of fluorinated azadienes, there is no general method for the synthesis of *N*-polyfluoroalkenyl azomethines.[1–3] Dehydrofluorination of fluorine-containing CH acids, which is employed for the formation of multiple bonds, is often performed with metal fluorides, KOH, NaOH, or tertiary amines.[4] For various reasons, however, these reagents cannot be used for dehydrofluorination of fluorinated azomethines.

The $BF_3 \cdot NEt_3$ complex is well known as a mild dehydrofluorinating agent, which provides the formation of a multiple bond in functionalized polyfluorinated compounds.[5] Using this complex in dehydrofluorination of a series of fluorine-containing azomethines (**1a—c**),[*] we obtained new fluorine-containing aza-1,3-dienes (**2a—c**), which can probably be used in cycloaddition reactions.



1a—c **2a—c**

X = H (**a**), Cl (**b**), CF_3 (**c**)

The dehydrofluorination of imine **1a** in the absence of a solvent leads to imine **2a** in 80% yield, and the dehydrofluorination of imidoyl chloride **1b** and imine **1c** on heating in dioxane results in azadienes **2b** and **2c** in 80% and 60% yields, respectively.

^1H and ^{19}F NMR spectra were recorded on a Bruker W-200SY spectrometer (^1H, 200.13 and ^{19}F, 188.29 MHz) in $CDCl_3$ with $SiMe_4$ (^1H NMR) and CF_3COOH (^{19}F NMR) as the standards.

***N*-α-Hydrohexafluoroisopropyltrifluoroethanimine (1a).**[6] Triethylamine (~0.01 g) was added to *N*-(2,2,2-trifluoroethyl)hexafluoropropan-2-imine (40.00 g, 0.162 mol) (exothermic reaction). The reaction mixture was kept at 20 °C for 1 h and distilled to give compound **1a** (36.00 g, 90%), b.p. 72 °C, n_D^{20} 1.2800. Found (%): C, 24.40; H, 0.55; N, 5.30; $C_5H_2F_9N$. Calculated (%): C, 24.29; H, 0.81; N, 5.67. ^{19}F NMR, δ: −4.7 (s, 3 F, CF_3); −8.1 (d, 6 F, $(CF_3)_2CH$). ^1H NMR, δ: 4.3 (septet, 1 H, $CH(CF_3)_2$, J = 6.13 Hz); 7.9 (br.s, 1 H, =CH).

***N*-α-Hydrohexafluoroisopropyltrifluoroacetimidoyl chloride (1b).** *N*-α-Hydrohexafluoroisopropyltrifluoroacetamide (84.00 g, 0.32 mol) was added to phosphorus pentachloride (133.40 g, 0.640 mol) at 10—15 °C. The reaction mixture was heated to 120 °C for 40 min and kept at this temperature for 4 h, collecting the fraction with b.p. < 85 °C. This fraction was then kept with ice (~200 g) for 1 h, washed with water (3×50 mL), dried with $MgSO_4$, and distilled to give compound **1b** (60.6 g, 60%), b.p. 62 °C, n_D^{20} 1.306. Found (%): C, 21.10; H, 0.30; N, 5.20; C_5HClF_9N. Calculated (%): C, 21.31; H, 0.36; N, 4.97. ^{19}F NMR, δ: −5.67 (s, 3 F, CF_3); −7.61 (d, 6 F, $(CF_3)_2CH$). ^1H NMR, δ: 5.0 (septet, 1 H, $CH(CF_3)_2$, J = 6.1 Hz).

***N*-α-Hydrohexafluoroisopropylhexafluoropropan-2-imine (1c)** has been previously obtained by another method.[7] Hexafluoroacetone (70.0 g, 0.422 mol) was added to α-hydrohexafluoroisopropylamine (70.40 g, 0.422 mol). The *N*-α-hydroxyhexafluoroisopropyl-α-hydrohexafluoroisopropylamine that formed was slowly added to 60% oleum (90 g) at 10 °C. Fractionation gave compound **1c** (81.00 g, 61%), b.p. 57 °C, n_D^{20} 1.271. Found (%): C, 22.75; H, 0.44; N, 4.20; $C_6HF_{12}N$. Calculated (%): C, 22.86; H, 0.32; N, 4.44. ^{19}F NMR, δ: −7.39 (d, 6 F, $(CF_3)_2CH$); −14.77 (q, 3 F, CF_3, J = 2.39 Hz); −7.13 (q, 3 F, CF_3, J = 7.2 Hz). ^1H NMR, δ: 4.9 (septet, 1 H, $CH(CF_3)_2$, J = 5.33 Hz).

***N*-Perfluoroisopropenyl-2,2,2-trifluoroethanimine (2a).** A mixture of azomethine **1a** (2.96 g, 0.012 mol) and the $BF_3 \cdot NEt_3$ complex (3.04 g, 0.018 mol) was heated in a closed vessel at 100—110 °C for 30 min. Twofold fractionation gave compound **2a** (2.18 g, 80%), b.p. 63 °C, n_D^{20} 1.312. Found (%): C, 26.53; H, 0.64; N, 6.10. C_5HF_8N. Calculated (%): C, 26.43; H, 0.44; N, 6.17. ^{19}F NMR, δ: −5.3 (s, 3 F, CF_3CH); −15.5 (dd, 3 F, $CF_3C{=}N$, J_1 = 26.0 Hz, J_2 = 8.0 Hz); −8.1 (dq, 1 F, CF_2, J_1 = 8.0 Hz, J_2 = 21.0 Hz); −2.7 (dq, 1 F, CF_2, J_1 = 21.0 Hz, J_2 = 26.0 Hz). ^1H NMR, δ: 7.7 (s, CH).

Perfluoro-*N*-isopropenylacetimidoyl chloride (2b). A mixture of azomethine **1b** (3.38 g, 0.012 mol), the $BF_3 \cdot NEt_3$ complex (3.04 g, 0.018 mol), and 3 mL of dry dioxane was heated in a closed vessel at 110—120 °C for 50 min. Twofold fractionation gave compound **2b** (2.51 g, 80%), b.p. 71 °C, n_D^{20} 1.3522. Found (%): C, 23.05; N, 5.20. C_5ClF_8N. Calculated (%): C, 22.94; N, 5.36. ^{19}F NMR, δ: −5.1 (s, 3 F, CF_3); −14.2 (dd, 3 F, CF_3, J_1 = 9.8 Hz, J_2 = 22.9 Hz); −1.8 (dq, 1 F, CF_2, J = 9.8 Hz); 9.7 (dq, 1 F, CF_2, J_1 = 9.8 Hz, J_2 = 22.9 Hz).

***N*-Perfluoroisopropenylhexafluoropropan-2-imine (2c).** A mixture of azomethine **1c** (3.78 g, 0.012 mol), the $BF_3 \cdot NEt_3$ complex (3.04 g, 0.018 mol), and 3 mL of dry

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[*] Azomethine **1a** was obtained by the known method.[6] Compound **1b** was synthesized for the first time by reaction of *N*-α-hydrohexafluoroisopropyltrifluoroacetamide with PCl_5. Azomethine **1c** was obtained by dehydration of the corresponding hemiaminal.

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dioxane was heated in a sealed glass tube at 120—130 °C for 60 min. Twofold fractionation gave compound **2c** (2.12 g, 60%), b.p. 60 °C, n_D^{20} 1.298. Found (%): C, 24.3; N, 4.93. $C_6F_{11}N$. Calculated (%): C, 24.41; N, 4.75. ^{19}F NMR, δ: −5.8 (br.d, 6 F, 2 CF_3, J = 4.8 Hz); −11.3 (dd, 3 F, $CF_3C{=}N$, J_1 = 20.1 Hz, J_2 = 8.3 Hz); 4.9 (m, 1 F, CF_2); 14.0 (dq, 1 F, CF_2, J_1 = 20.1 Hz, J_2 = 15.0 Hz).

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Fluoride ion-catalyzed condensation of perfluoroisobutene with diethyl azodicarboxylate

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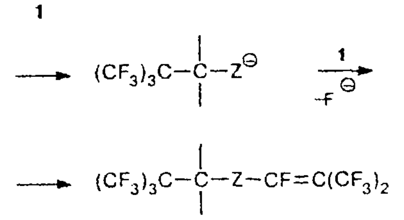
Reactions of perfluoroisobutene (**1**) with compounds having electrophilic multiple bonds catalyzed by fluoride anions can occur as the conjugated nucleophilic addition with the perfluoro-*tert*-butyl anion as a nucleophile and the second molecule of olefin **1** as an electrophile in the final stage of the reaction (Scheme 1).

Scheme 1

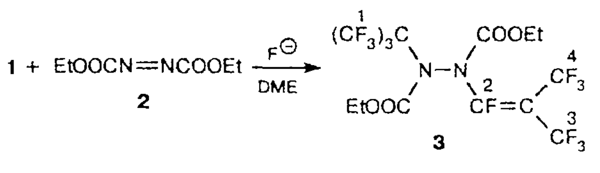


This reaction scheme, implying the formation of intermediate C- or O-anions, occurs in the reaction of olefin **1** with acrylonitrile, olefins $CF_2{=}CFX$ (X = F, CF_3, and OCF_3), or aromatic aldehydes.[1–3]

It is shown that the reaction of compound **1** with diethyl azodicarboxylate (**2**) (in this case, *via* an N-anion) also follows a similar pathway leading to a derivative of 1,2-hydrazinodicarboxylic acid (**3**) in high yield (Scheme 2).

The reaction discovered opens a new route to hydrazine derivatives containing the $(CF_3)_3C$ group at the nitrogen atom (*cf.* Ref. 4).

Scheme 2



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