From the data of Table 1 it follows that a decrease in the angle between the planes of the double bonds brings about significant attenuation of TBI, whereas TSI is little affected. Since the through-bond interaction is greatest in the flat conformation, it is a supplementary flattening factor, and, in parallel with steric effects, has significant influence on the equilibrium structure and conformational flexibility of the 1,4-cyclohexadiene molecule.

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Received May 12, 1994

Monoamination of internal fluoroolefins

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Perfluoro-2-methyl-2-pentene and perfluoro-1-methylcyclopentene react with ammonia or aniline under controlled conditions to give monoamination products.

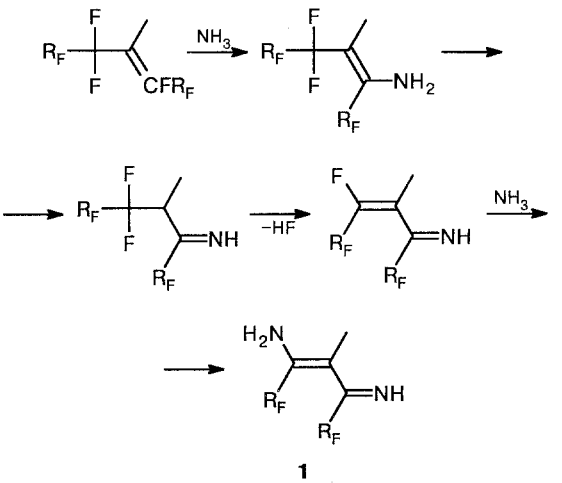
Key words: internal fluoroolefins, amination; fluorinated enamines, fluorinated imines, synthesis.

Reactions of internal fluoroolefins with ammonia usually occur as vinylic substitution followed by enamine-imine isomerization and dehydrofluorination giving rise to imino-enamines (**1**) or the products of their further transformations[1–4] (Scheme 1).

The products of the monoamination of perfluoro-2-butene or isomeric C_8F_{16}-olefins by ammonia have also been reported.[5,6]

We found that perfluoro-2-methyl-2-pentene (**2**) also gives a monosubstituted product, *viz.*, imine **3a**, in a moderate yield under controlled conditions (0—20 °C, calculated amount of ammonia). Similarly, anil **3b** and enamine **5** were prepared from olefin **2** and aniline or

Scheme 1

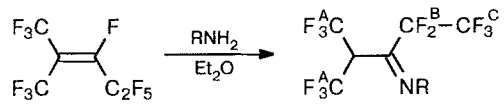


1

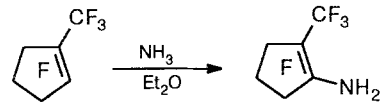
† Deceased in 1994.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 9, pp. 1678—1679, September, 1994.

perfluoro-1-methylcyclopentene (**4**) and ammonia, respectively.

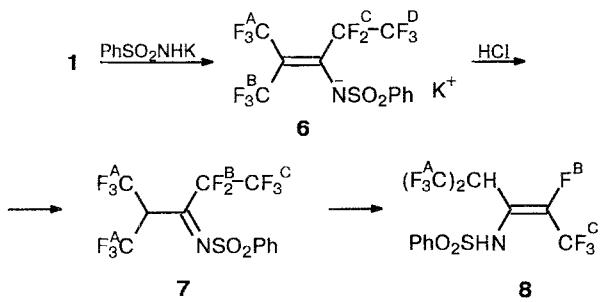


2 **3a,b**
a: R = H
b: R = Ph



4 **5**

However, one cannot entirely avoid further transformations of compounds **3a** and **5** under the action of NH_3, despite very mild conditions. This is apparently associated with the fact that the rates of substitution of the vinylic fluorine atom and subsequent dehydrofluorination are comparable, which results in the formation of polyamination products. The latter have been synthesized earlier[2,4] by the interaction of compounds **2** or **4** with excess ammonia. However, the reaction of fluoroolefin **2** with potassium benzenesulfonamidate proceeds in an uncomplicated manner to afford the potassium salt of the mesomeric anion **6** in a high yield. This salt can be transformed into sulfonylimine **7** by the usual method.[7]



6 **7** **8**

The structures of the compounds obtained were confirmed by spectral methods. In the case of imine **3a**, the structure was also confirmed by its acid hydrolysis into ketone $(CF_3)_2CHC(O)C_2F_5$. The reductive defluorination of sulfonylimine **7** into enamine **8** by the action of metallic Mg in THF[8] was also carried out.

Experimental

^1H and ^{19}F NMR spectra were recorded on a Bruker-200 SY instrument at 200 MHz and 188.3 MHz, respectively, in CCl_4 relative to tetramethysilane and trifluoroacetic acid as external standards, respectively. IR spectra were recorded on a UR-20 spectrophotometer. Mass-spectra were obtained on a VG-7070E spectrometer at the ionization potential 70 eV.

2-Hydroperfluoro-2-methyl-3-pentaneimine (3a). Ammonia (1.5 g) was passed through a solution of olefin **2** (11.4 g) in absolute ether (20 mL) at 0 °C with stirring. The mixture was then heated to 20 °C and kept for 3 h. The solvent and volatile products were evaporated *in vacuo* (10 Torr) at 100 °C, the distillate was redistilled to give 5.3 g of a fraction with b.p. 70—80 °C, which contained, according to GLC analysis, ether (3 %), $(CF_3)_2CHC_3F_7$ (7 %), and imine **3a** (90 %). Rectification of this fraction gave pure imine **3a** as a mixture of *syn*- and *anti*-isomers, b.p. 72—78 °C. Found (%): C, 23.97; H, 0.72; F, 70.03. $C_6H_2F_{11}N$. Calculated (%): C, 24.24; H, 0.67; F, 70.34. IR, ν/cm^{-1}: 1670 (C=N); 2900 (CH); 3200—3320 (NH). ^{19}F NMR, δ: −14.1 and −14.0 (both m, F^A); 2.5 and 4.0 (both m, F^C); 38.0 and 43.2 (both m, F^B). MS, *m/z* (I_{rel} (%)): 278 $[M-F]^+$ (6), 178 $[M-C_2F_5]^+$ (100), 146 $[C_2F_5CNH]^+$ (49.5), 69 $[CF_3]^+$ (50).

***N*-[2,2,3,3,3-Pentafluoro-1-(2,2,2-trifluoro-1-trifluoromethyl)ethylpropylidene]aniline (3b).** A solution of aniline (2.1 g) and olefin **2** (13.5 g) in absolute ether (30 mL) was kept for 4 h at 20 °C, then washed with dilute HCl (1:5), dried with $MgSO_4$, and distilled to afford 3 g of a fraction with b.p. 65—67 °C (12 Torr), which contained 84 % imine **3b** (GLC analysis). Pure **3b**, n_D^{20} 1.3872, was isolated by preparative GLC. Found (%): C, 38.50; H, 1.68; F, 56.60. $C_{12}H_6F_{11}N$. Calculated (%): C, 38.60; H, 1.61; F, 56.03. IR, ν/cm^{-1}: 1680 (C=N). ^1H NMR, δ: 4.9 (sept, CH); 7.0—7.8 (m, Ph). ^{19}F NMR, δ: −16.1 (dt, F^A); 3.0 (s, F^C); 34.8 (sept, F^B, $J_{FA,FB}$ = 11 Hz).

2-Aminoperfluoro-1-methylcyclopentene (5). Ammonia (1.4 g) was passed through a solution of olefin **4** (11.9 g) in absolute ether (25 mL) at 0 °C. The mixture was heated to 20 °C, and the ether and volatile products were evaporated at 100 °C (10 Torr). Subsequent distillation gave 6.8 g (57 %) of enamine **5**, b.p. 70—72 °C (32 Torr), n_D^{20} 1.3496. Found (%): C, 27.70; H, 0.79; F, 65.91; N, 5.66. $C_6H_2F_9N$. Calculated (%) : C, 27.79; H, 0.77; F, 66.02; N, 5.40. ^1H NMR, δ: 4.9 (br.s). ^{19}F NMR, δ: −18.6 (m, CF_3); 27.0, 42.1, and 54.2 (all m, CF_2). MS, *m/z* (I_{rel} (%)): 259 $[M]^+$ (100), 240 $[M-F]^+$ (77.2).

***N*-[2,2,3,3,3-Pentafluoro-1-(2,2,2-trifluoro-1-trifluoromethyl)ethylpropylidene]benzenesulfonamide (7).** Olefin **2** (17 g) was added dropwise to a suspension of potassium benzenesulfonamidate (5 g) in absolute monoglyme (40 mL) with stirring and cooling, so that the temperature of the reaction mixture did not exceed 35 °C. The resultant homogenous solution was stirred for 1 h. Concentration of the mixture afforded a yellow solution of salt **6** in monoglyme. ^{19}F NMR, δ: −26.2 (tq, F^A); −21.5 (q, F^B); 1.0 (s, F^D); 34.6 (q, F^C, $J_{FA,FB}$ = 9 Hz, $J_{FA,FC}$ = 20 Hz). After evaporation of the solvent *in vacuo*, absolute CH_2Cl_2 was added to the residue, and dry HCl was passed through the mixture until saturation. The precipitate was then filtered off, and distillation of the filtrate afforded 9.2 g (82 %) of imine **7**, b.p. 78—80 °C (2 Torr). Found (%): C, 32.50; H, 1.34; F, 48.01. $C_{12}H_6F_{11}NO_2S$. Calculated (%) : C, 32.95; H, 1.37; F, 47.82. IR, ν/cm^{-1}: 1665 (C=N). ^1H NMR, δ: 6.5 (sept, CH); 7.8—8.3 (m, Ph). ^{19}F NMR, δ: −17.1 (dt, F^A); 3.2 (s, F^C); 35.5 (sept, F^B, $J_{FA,FB}$ = 11 Hz, $J_{FA,CH}$ = 7.5 Hz).

4-Hydroperfluoro-4-methyl-3-phenylsulfonamido-2-pentene (8). $HgCl_2$ (0.3 g) was added to Mg chips (0.7 g) in absolute THF (35 mL) under Ar with stirring. After the exothermic reaction was finished, a solution of imine **7** (8.8 g) in THF (10 mL) was added dropwise at a temperature below 35 °C. After 1 h, the reaction mixture was poured into cooled dilute HCl (1:5), the oil that precipitated was extracted with ether, and the extract was dried with $MgSO_4$. Distillation afforded

4.3 g (49 %) of enamide **8**, b.p. 135—145 °C (2 Torr), m.p. 82—84 °C. Found (%): C, 34.37; H, 1.54; F, 45.17. $C_{12}H_7F_{10}NO_2S$. Calculated (%): C, 34.36; H, 1.67; F, 45.34. Raman spectrum, ν/cm^{-1}: 1695 (C=C). ^1H NMR, δ: 5.1 (sept, CH); 7.3 (s, NH); 7.9—8.2 (m, Ph). ^{19}F NMR, δ: −14.3 (dd, F^A); −10.5 (d, F^C); 46.3 (m, F^B, $J_{FA,FB}$ = 17 Hz, $J_{FC,FB}$ = 9 Hz, $J_{FA,CH}$ = 8 Hz).

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Received June 15, 1994