Reaction of perfluoro-2-methylpent-2-ene with azoles

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Perfluoro-2-methylpent-2-ene reacts with pyrazole, imidazole, 1,2,4-triazole, and benzotriazole to give products of the replacement of the vinylic fluorine atom. In the case of imidazole, the product of allylic fluorine substitution, 1,3-bisimidazolylperfluoro-2-methylpent-2-ene, is also formed. The structures of the products were confirmed by spectral data.

Key words: perfluoro-2-methylpent-2-ene, NMR spectroscopy, nucleophilic substitution, 1-(perfluoro-1-ethyl-2-methylprop-1-enyl)imidazole, -pyrazole, -1,2,4-triazole, -benzotriazole.

The reactions of internal perfluoroalkenes with secondary amines are known[1] to give not only the products of the replacement of the vinylic fluorine atom but also enamines derived from a terminal perfluoroalkene. It has been assumed that this is due to the fact that under the action of amines, internal perfluoroalkenes isomerize to give terminal perfluoroalkenes and that the type of amine is significant for this process. In fact, diethylamine yields enamine derived from the isomerized perfluoroalkene,[1] whereas pyrrolidine[2] and piperidine[3] lead to mixtures of two enamines, whose ratio depends on the solvent. In the case of lactams (α-piperidone, α-pyrrolidone, caprolactam, *etc.*), substitution of the vinylic fluorine atom occurs.[4–6] It may be suggested that these N-nucleophiles do not catalyze isomerization.

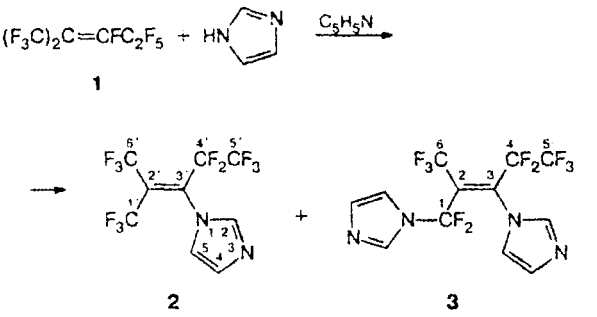
The purpose of this work is to study the reactions of perfluoro-2-methylpent-2-ene (**1**) with some azoles (pyrazole, imidazole, 1,2,4-triazole, and benzotriazole), which are weak bases, but are still stronger than carboxamides.

The reaction of perfluoroalkene **1** with imidazole in pyridine yields the product of the vinylic substitution of fluorine, *viz.*, *N*-(perfluoro-1-ethyl-2-methylprop-1-enyl)imidazole (**2**), and the product of subsequent allylic substitution of the fluorine atom in the CF_3 group, *viz.*, 1,3-bisimidazolyl-2-methylperfluoropent-2-ene (**3**) (Scheme 1).

Apparently, the basicities of imidazole and pyridine are insufficient to ensure isomerization of compound **1** to 2-methylperfluoropent-1-ene; therefore, no products of its reaction with nucleophiles were detected.

The structures of compounds **2** and **3** were confirmed by spectroscopic data, which were interpreted taking into account the available information on the structures of compounds of this type.

Scheme 1



To direct the reaction to the formation of only compound **2**, the vinylic fluorine atom was temporarily replaced by the easily leaving Et_3N group. Previously,[7] (trifluoro-1-pentafluoroethyl-2-trifluoromethylprop-1-enyl)triethylammonium fluoride (**4**) was obtained by the reaction of compound **1** with Et_3N. Recently[8] it was shown that when salts of this type react with dialkylamines, the Alk_3N^+ group is replaced by a dialkylamino group. In the reaction with pyridine, compound **1** does not form salts of type of **4** (^{19}F NMR spectrum).

We found that salt **4** prepared by the known procedure[7] reacts with imidazole, pyrazole, 1,2,4-triazole, and benzotriazole to give products **2**, and **5**—**7** respectively (Scheme 2). In the case of imidazole, compound **3** can also be isolated; however, the yield of product **2** is higher and the yield of product **3** is lower than those obtained according to Scheme 1.

Evidently, product **3** is formed from compound **2** by allylic substitution of a fluorine atom in the CF_3 group (Scheme 3). Enamine **2** is actually converted into com-

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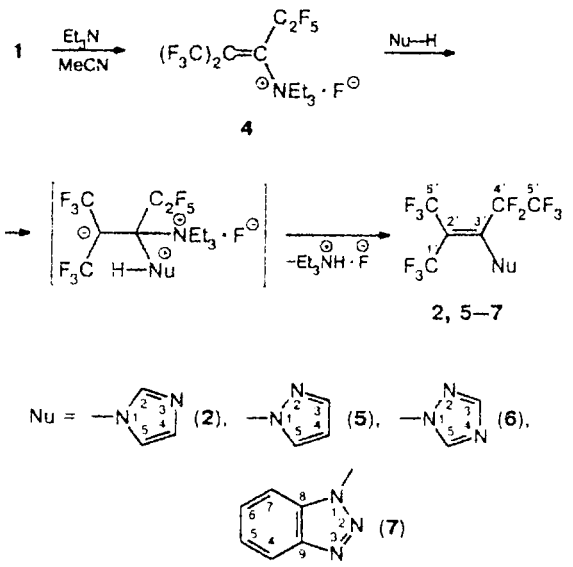
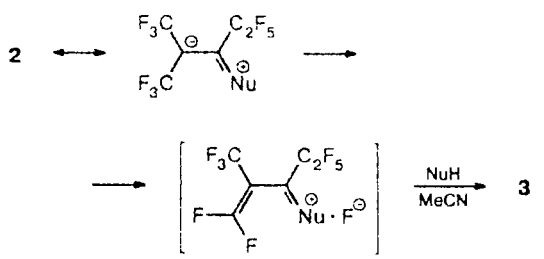
Scheme 2



pound **3** in 37% yield in the presence of an equimolar amount of imidazole in MeCN, whereas compound **2** itself does not change when heated in MeCN (4 h at 70 °C).

Scheme 3



Experimental

^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a Bruker WP 200 SY spectrometer (200, 50, and 188 MHz, respectively) using tetramethylsilane and C_6F_6 as the internal standards. IR spectra were recorded on a Specord M-80 spectrophotometer (CCl_4); and mass spectra were obtained on a VG 707 OE GC/MS spectrometer (with an energy of the ionizing electrons of 70 eV).

Reaction of compound 1 with imidazole. ***A.*** Compound **1** (15 g, 50 mmol) was added to a solution of imidazole (3.4 g, 50 mmol) in 100 mL of pyridine at 20 °C. The mixture was stirred at 60 °C for 1 h and poured into water; the organic layer was separated, washed with 5% HCl and water, and dried with $MgSO_4$. Evaporation of the solvent yielded 17.5 g of a mixture whose distillation gave 6 g (34.5%) of *N*-(perfluoro-1-ethyl-2-methylprop-1-enyl)imidazole (**2**), b.p. 76—78 °C (20 Torr). IR (CCl_4), ν/cm^{-1}: 3110 (C—H); 1635 (C=C); 1465 (N=C); 1190—1230 (C—F). MS, m/z (I_{rel}(%)): 348 $[M]^+$ (100), 329 $[M-F]^+$ (35), 279 $[M-CF_3]^+$ (11), 260 $[M-CF_3-F]^+$ (3.7), 290 (30), 203 (29), 202 (11), 182 (11), 69 $[CF_3]^+$ (46), 52 $[CHF_2]^+$ (13). Found: m/z = 348.01270. $C_9H_3F_{11}N_2$. Calculated: m/z = 348.01205. ^{1}H NMR (CD_3CN), δ: 7.14 (s, H(2)); 7.80 and 7.87 (both d, H(4) and H(5), J = 7.0). ^{19}F NMR (CD_3CN), δ: 107.0 (3 F, FC(1′), $J_{F(1'),F(5')}$ = 9 Hz; $J_{F(1'),F(4')}$ = 18 Hz; $J_{F(1'),F(6')}$ = 9 Hz); 103.6 (3 F, FC(6′), $J_{F(6'),F(1')}$ = 9 Hz); 82.9 (3 F, FC(5′), $J_{F(5'),F(1')}$ = 9 Hz); 52.3 (2 F, FC(4′), $J_{F(4'),F(1')}$ = 18 Hz). ^{13}C NMR (CD_3CN), δ: 139.4 (C(3′), $^2J_{C,F}$ = 28.3 Hz); 139.8 (C(2)); 132.1 (C(5)); 129.9 (C(2′), $^2J_{C,F}$ = 34.5 Hz); 122.4 (C(4)); 121.0 (C(6′), $^1J_{C,F}$ = 277.9 Hz); 120.0 (C(1′), $^1J_{C,F}$ = 276 Hz); 119.0 (C(5′), $^1J_{C,F}$ = 287.9 Hz, $^2J_{C,F}$ = 35.2 Hz); 108.6 (C(4′), $^1J_{C,F}$ = 261.5 Hz, $^2J_{C,F}$ = 40.4 Hz). Vacuum sublimation at 130 °C (0.8 Torr) of the residue after distillation of compound **2**, and subsequent recrystallization from CCl_4 gave 4.5 g (22.7%) of 1,3-bisimidazolylperfluoro-2-methylpent-2-ene (**3**), m.p. 140—142 °C. IR (CCl_4), ν/cm^{-1}: 3100 (C—H); 1625 (C=C); 1415, 1495 (N=C); 1120—1250 (C—F). MS, m/z (I_{rel}(%)): 396 $[M]^+$ (100), 377 $[M-F]^+$ (5), 327 $[M-CF_3]^+$ (1.3), 329 $[M-C_3H_3N_2]^+$ (8), 309 $[M-CF_3-F]^+$ (11), 277 $[M-C_2F_5]^+$ (12.9), 120 $[M-HC_2F_5]^+$ (18.8), 119 $[C_2F_5]^+$ (7.4), 52 $[CHF_2]^+$ (21.9). Found: m/z = 396.04405. $C_{12}H_6F_{10}N_4$. Calculated: m/z = 396.04326. ^{1}H NMR (CD_3CN), δ: 7.67 and 6.88 (both d, H(5′), H(4′), J = 7.0 Hz); 7.17 (s, H(2′)). ^{19}F NMR (CD_3CN), δ: 108.4 (3 F, FC(6)); 83.3 (3 F, FC(5); 62.5 (2 F, FC(4)); 42.8 (2 F, C(1)).

B. A mixture of compound **1** (15 g, 50 mmol) and Et_3N (5 g, 50 mmol) in 20 mL of MeCN was stirred for 1.5 h at 55 °C. The mixture was cooled to 20 °C, and imidazole (2.4 g, 50 mmol) was added. The reaction mixture was stirred at 20 °C for 0.5 h and at 55 °C for 1.5 h, cooled, poured into water, and extracted with ether. The extract was dried with $MgSO_4$. Distillation gave 7.46 g (43%) of compound **2**, b.p. 76—78 °C (20 Torr); sublimation of the distillation residue at 130 °C (0.8 Torr) gave 2.28 g (11.5%) of compound **3**. Judging by their spectra, compounds **2** and **3** were similar to those prepared by procedure ***A***.

***N*-(Perfluoro-1-ethyl-2-methylprop-1-enyl)pyrazole (5).** A mixture of compound **1** (15 g, 50 mmol), Et_3N (5 g, 50 mmol), and 20 mL of MeCN was stirred for 1.5 h at 50 °C; pyrazole (3.4 g, 50 mmol) in 35 mL of MeCN was added dropwise over a period of 1 h, and the mixture was heated to 80 °C, kept for 3 h, and left overnight. Then the reaction mixture was poured into water and extracted with ether; the extract was washed successively with saturated solutions of $NaHCO_3$ and NaCl (100 mL), and the ethereal layer was separated. The extract was dried with $MgSO_4$ and treated with activated carbon (grade "C", 0.5 g). Distillation gave 7.03 g (40%) of compound **5**, b.p. 70—72 °C (20 Torr). IR (CCl_4), ν/cm^{-1}: 3110 (C—H); 1625 (C=C); 1515 (N=C); 1180—1240 (C—F). MS, m/z (I_{rel}(%)): 348 $[M]^+$ (100), 329 $[M-F]^+$ (51.9), 281 $[M-C_3H_2N_2]^+$ (4.3), 279 $[M-CF_3]^+$ (52.5), 229 $[M-C_2F_5]^+$ (19.6), 209 $[M-C_2F_5-HF]^+$ (18.5), 119 $[C_2F_5]^+$ (5.1), 69 $[CF_3]^+$ (45.4), 52 $[CHF_2]^+$ (21.2). Found: m/z = 348.00994. $C_9H_3F_{11}N_2$. Calculated: m/z = 348.01205. ^{1}H NMR (CD_3CN), δ: 6.53 (dd, H(4), J = 2.8 Hz, J = 1.5 Hz); 7.70 (d, H(3), J = 1.5 Hz); 7.75 (t, H(5), $^3J_{H,H}$ = $^5J_{H,F}$ = 2.8 Hz). ^{19}F NMR (CD_3CN), δ: 106.8 (qqt, 3 F, FC(1′), J = 10 Hz, J = 18 Hz, J = 8 Hz); 101.8 (q, 3 F, FC(6′), J = 10 Hz); 82.0 (q, 3 F, FC(5′), J = 18 Hz); 50.6 (q, 2 F, FC(4′), J = 8 Hz). ^{13}C NMR (CD_3CN), δ: 142.4 (C(3)); 138.6 (C(2′), $^2J_{C,F}$ = 27.5 Hz); 131.3 (C(5)); 126.8 (C(3′), $^2J_{C,F}$ = 32.5 Hz); 118.6 (C(1′), $^1J_{C,F}$ = 276.7 Hz); 118.2

(C(6'), $^1J_{C,F}$ = 276.6 Hz); 116.5 (C(5'), $^1J_{C,F}$ = 288.5 Hz, $^2J_{C,F}$ = 35.5 Hz); 109.4 (C(4)); 108.8 (C(4'), $^1J_{C,F}$ = 261.6 Hz, $^2J_{C,F}$ = 40.1 Hz).

1-(Perfluoro-1-ethyl-2-methylprop-1-enyl)-1,2,4-triazole (6). A mixture of compound **1** (15 g, 50 mmol), Et_3N (5 g, 50 mmol), and 25 mL of MeCN was stirred at 55 °C for 1.5 h, and cooled to 20 °C; 1,2,4-triazole (3.45 g, 50 mmol) was added. Then the mixture was stirred at 55 °C for 2 h, poured into water, washed with 10% HCl and water, and extracted with ether. The extract was dried with $MgSO_4$. Distillation gave 4.76 g (17.5%) of compound **6**, b.p. 72—75 °C (30 Torr). IR (CCl_4), ν/cm^{-1}: 3120 (C—H); 1650 (C=C); 1505 (N=C); 1190—1250 (C—F). MS, m/z (I_{rel}(%)): 349 $[M]^+$ (49.6), 330 $[M-F]^+$ (21.1), 323 $[M-CN]^+$ (27.7), 295 $[M-N_2-CN]^+$ (38.8), 276 $[M-N_2-CN-F]^+$ (19.9), 119 $[C_2F_5]^+$ (100), 69 $[CF_3]^+$ (73.6), 50 $[CF_2]^+$ (2.2). Found: m/z = 349.00941. $C_8H_2F_{11}N_3$. Calculated: m/z = 349.00729. ^1H NMR (CD_3CN), δ: 8.18 and 8.69 (both s, H(3), H(5)). ^{19}F NMR (CD_3CN), δ: 106.7 (qqt, 3 F, FC(1'), J = 10 Hz, J = 8 Hz, J = 20 Hz); 102.4 (q, 3 F, FC(6'), J = 10 Hz); 82.6 (q, 3 F, FC(5'), J = 8 Hz); 51.2 (q, 2 F, FC(4'), J = 20 Hz). ^{13}C NMR (CD_3CN), δ: 154.8 (C(5)); 147.5 (C(3)); 138.8 (C(3'), $^2J_{C,F}$ = 28.7 Hz); 132.4 (C(2'), $^2J_{C,F}$ = 34.8 Hz); 120.8 (C(1'), $^1J_{C,F}$ = 278 Hz); 120.4 (C(6'), $^1J_{C,F}$ = 276.8 Hz); 119.1 (C(5'), $^1J_{C,F}$ = 287 Hz, $^2J_{C,F}$ = 35.1 Hz); 111.2 (C(4'), $^1J_{C,F}$ = 261.3 Hz, $^2J_{C,F}$ = 41.4 Hz).

1-(Perfluoro-1-ethyl-2-methylprop-1-enyl)benzotriazole (7). A mixture of compound **1** (6.0 g, 20 mmol), Et_3N (2.02 g, 20 mmol), and 10 mL of MeCN was stirred at 50 °C for 2 h and cooled to 10 °C. Benzotriazole (2.38 g, 20 mmol) was added, and the mixture was stirred at 20 °C for 4 h and poured into water. The product was extracted with ether, the extract was dried with $MgSO_4$ and distilled to give 3.38 g (42%) of compound **7**, b.p. 51—52 °C (0.03 Torr). MS, m/z (I_{rel} (%)): 399 $[M]^+$ (19.62), 371 $[M-N_2]^+$ (40.04), 302 $[M-N_2-CF_3]^+$ (100), 252 $[M-N_2-C_2F_5]^+$ (98.43), 232 (13.57), 207 (20.94), 183 (12.21), 157 (16.36), 100 $[CF_2=CF_2]^+$ (0.64), 95 $[CF_3CN]^+$ (49.56), 90 $[NC_6H_4]^+$ (33.56), 76 $[C_6H_4]^+$ (23.09), 69 $[CF_3]^+$ (26.95), 28 $[N_2]^+$ (8.50). Found: m/z = 399.02183. $C_{12}H_4F_{11}N_3$. Calculated: m/z = 399.02294. IR (CCl_4), ν/cm^{-1}: 1650 (C=C); 1315 (C—N); 1150—1250 (C—F). ^1H NMR (CD_2Cl_2), δ: 8.09 (d, 1 H, C(4), J = 8 Hz); 7.78 (t, 1 H, C(5), J = 8 Hz); 7.42 (t, 1 H, C(6), J = 8 Hz); 7.40 (d, 1 H, C(7), J = 8 Hz). ^{19}F NMR (CD_2Cl_2), δ: 106.6 (3 F, CF_3); 102.4 (3 F, CF_3); 82.8 (3 F, CF_3); 54.9 and 50.9 (2 F, CF_2, AB-system, $^3J_{F,F}$ = 286.1 Hz). ^{13}C NMR (CD_2Cl_2), δ: 145.6 (C(8)); 136.9 (C(3'), $^2J_{C,F}$ = 29.7 Hz); 133.9 (C(9)); 131.7 (C(2'), $^2J_{C,F}$ = 35.3 Hz); 129.5 (C(6)); 124.7 (C(5)); 119.8 (C(4)); 119.1 (C(1'), $^1J_{C,F}$ = 278.1 Hz); 118.6 (C(6'), $^1J_{C,F}$ = 277.1 Hz); 117.3 (C(5'), $^1J_{C,F}$ = 288.2 Hz, $^2J_{C,F}$ = 35.8 Hz); 110.5 (C(4'), $^1J_{C,F}$ = 260.7 Hz, $^2J_{C,F}$ = 40.9 Hz); 109.8 (C(7)).

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