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Adducts of pyrrole with fluorinated olefines

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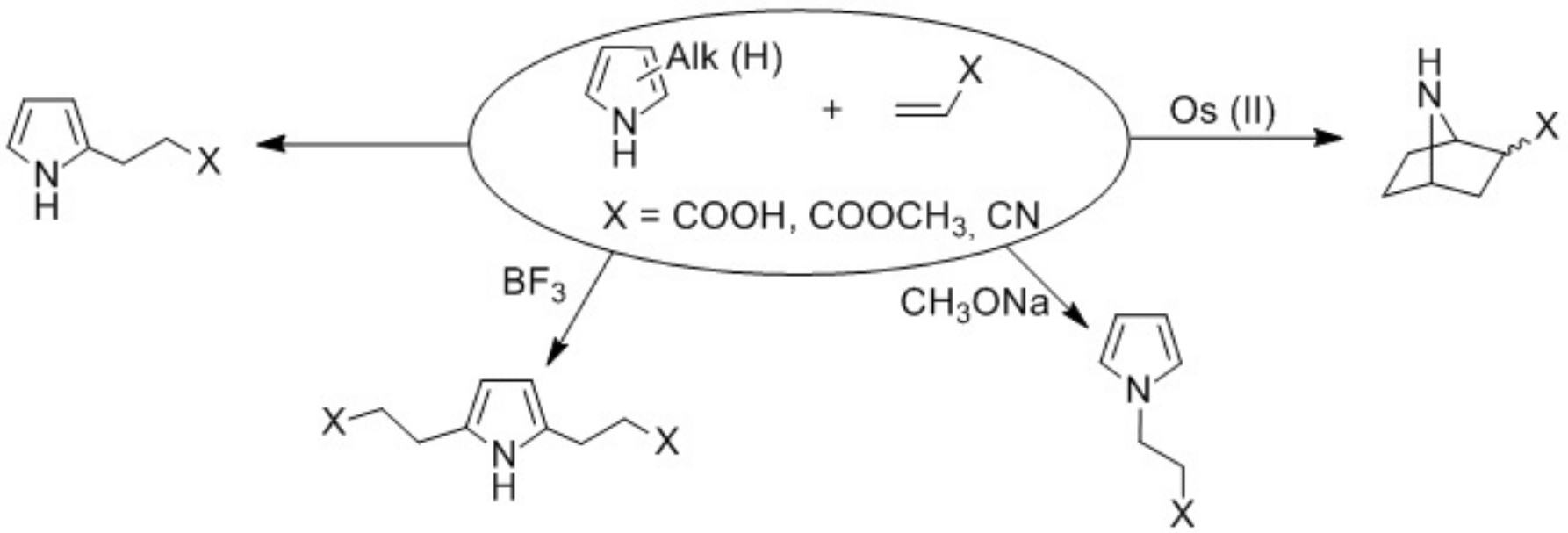
Abstract:In the reaction methyl perfluoroacrylate with pyrrole produced methyl ether of 2,3,3-trifluoro-3-(1H-pyrryl-2в Ъ™)-propionic acid, as the result additions in O±-position of pyrrole. But the reaction pyrroles with terminal fluorolefins gives only compounds [2+4]-cycloadditions, as the mixing exo- and endo-stereoisomers. We did to isolation of stereo-isomers with a help flash-chromatography on spherical particles (sizeB -B 15Ojm) silica gels with chloroform (or dichloromethane) as eluent. In the reaction pyrroles with perfluoroallylbenzene has been tetracyclic compounds: perfluorobenz[1,2-e]-2,2,3-trifluoro-6-azatricyclo-[4.3.0.0^{3,7}]nonane-8.

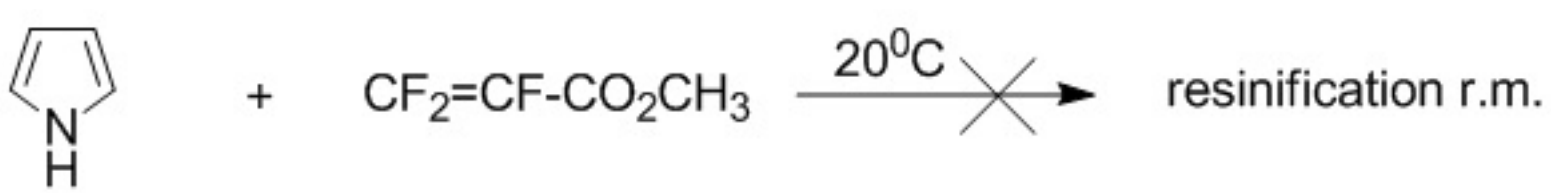
Keywords: Pyrrole, methyltrifluoroacrylate, terminal fluoroelefins, [2+4]-cycloaddition, 5,5,6-trifluoro-6-exo-polyfluoroalkyl- and 5,5,6-trifluoro-6-endo-polyfluoroalkyl-7-azabicyclo-[2.2.1]hept-2-enes, flash-chromatography, NMR-spectroscopy ^{1}H, ^{19}F Pë ^{13}C, HSQC and COSY-spectrum, MS-spectroscopy.

However [1] it was shown that, a reaction pyrrole and polyalkylpyrroles with acrylic acid and it derivatives give ambiguous results: addition acrylates in O±-position of pyrrolesB [2]; double addition in O±B and O ±в Ъ™B positions (by catalysis acids of Lewis)B [3]; addition on the atom of nitrogen pyrroles (by basic catalysis)B [4] and cycloadditions (catalysis by salts ofB Os^{2+})B [5].

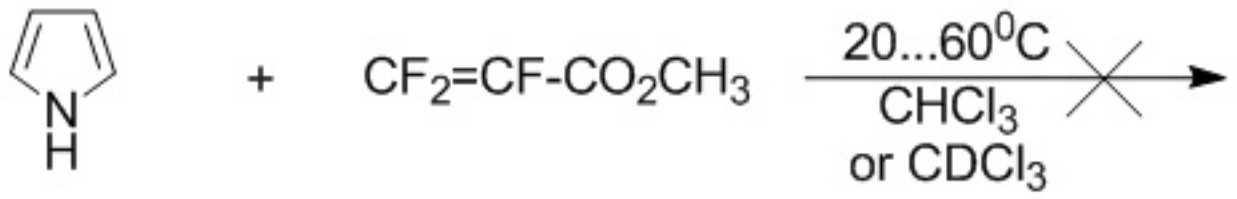


At the same time the research of reactionary ability of fluorinated acrylates, being representatives of functionally substituted for olefins, with an pyrrole which are know only in a few example [1]. The derivatives of pyrrole are presented by the considerable assortment of representatives of bioactive substances of the widest spectrum of action. Itв Ъ™s interestly to estimate possibility of receipt fluorinated adducts pyrroles as accessible precursors of new bioactive substances.

The reaction pyrrole with methyl perfluoroacrylates without solvents by 20B°C going to polymerization in the reaction mixture.

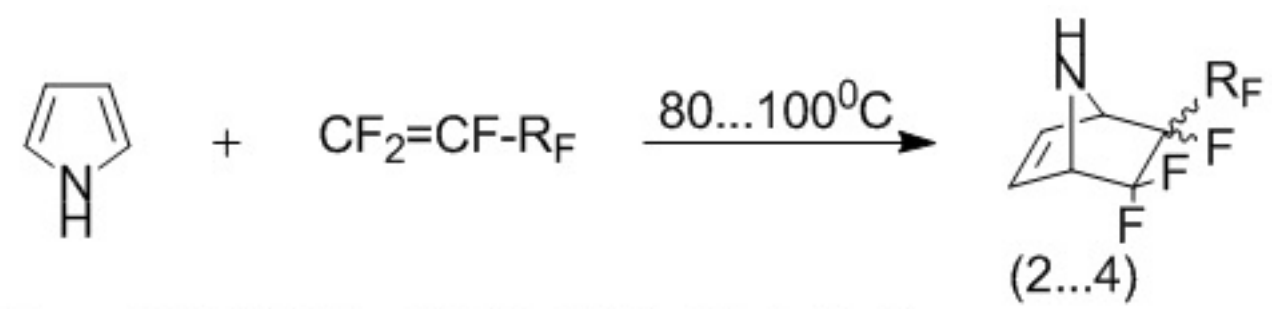


At the same time mixture of pyrrole (1M) and methyl ether of acrylic acidB (1M) in a chloroform does not change in the interval of temperatures from 20 to 60B°C during a 7 days.



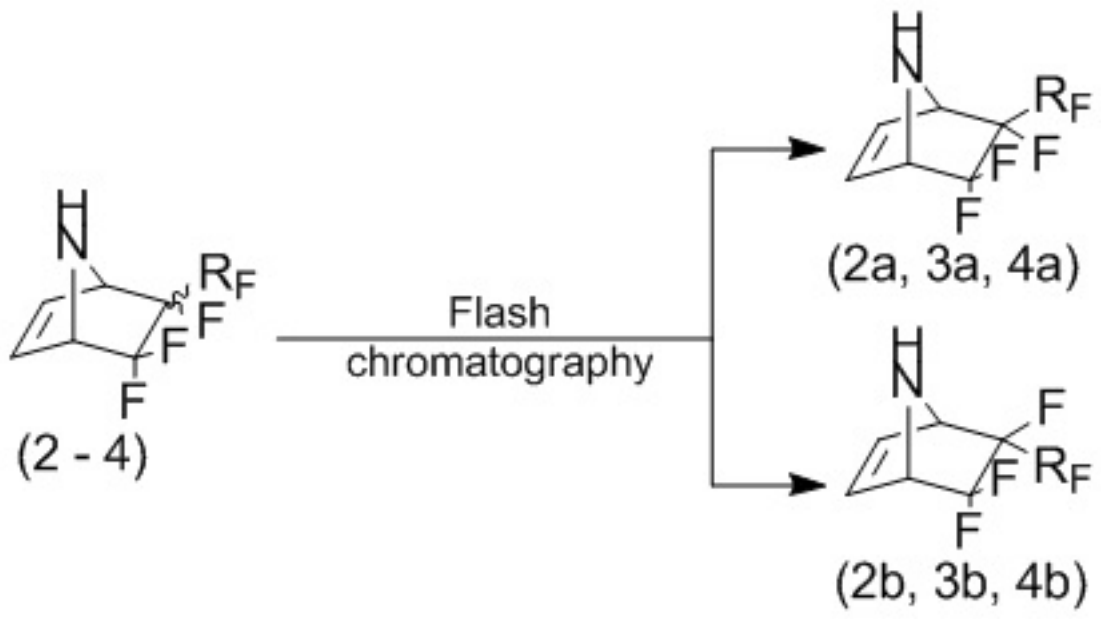
Heating of the same mixture of reagents in a dichloromethane by reflux during a 10 days with subsequent factious distillation of reactionary mass in vacuum allows to get methyl ether of 2,3,3-trifluoro-3-(1HB pyrrylB 2вЂ™)-propionic acid (1), being the product of additions of methyl perfluoroacrylate in O±-position of pyrroles.

By changing terminal perfluorolefins (if exchange carboxylic group on perfluoroalkyl group), between pyrroles and olefins has been only compounds (2-4), as products of [2+4]-cycloaddition. So, co-operation of pyrrole with such a perfluorolefins, as 4-hydroperfluorobut-1-ene, 4B chloroheptafluorobut-1-ene and perfluoroallylbenzene, has been only adducts (2-4). Thus, compounds (2-4) appear as mixture of the stereoisomeres relatively perfluoroakyl-groups.



R_F = -CF_2CF_2H (2), -CF_2CF_2Cl (3), -$CF_2C_6F_5$ (4)

Attempt to highlight the individual adducts (2-4) as stereoisomers by fractional distillation and crystallization of the hydrochlorides has failed. Therefore, experiments were carried out on the selection of separation conditions stereoisomeric compounds (2-4) by flash chromatography. It was found that the use of sorbent spherical silica gel (particle size 15B Ojm) and eluent is chloroform (or dichloromethane), allows to separate quantitatively stereoisomeric mixture of compounds (2-4).



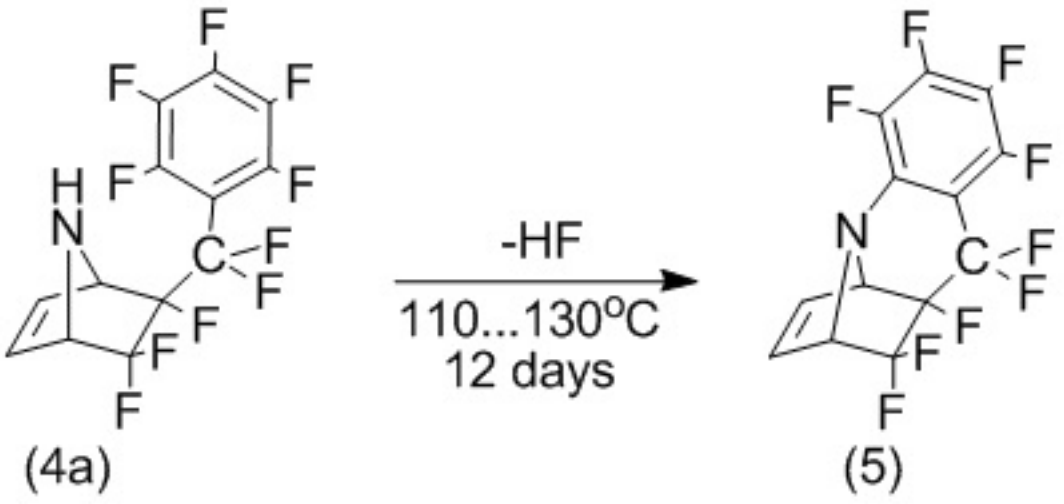
Interestingly, reacting pyrrole with 4-chloroheptafluorobut-1-ene and 4-hydroperfluorobut-1-ene at a higher temperature (130B°C) leads only to an increase in product yield and reduce resinification adducts (2, 3). The ratio of the stereoisomers (relative fluoroalkyl group) did not significantly change.

In the case of heating the mixture of pyrrole and perfluoroallylbenzene at 130B°C it begins to apper a mixture of exo-perfluorobenzyl-stereoisomers (4a) and endo- perfluorobenzyl-stereoisomers (4b). After 20B hours, according to date GC-MS, begins conversion of compound (4a) to form product of elimination of one molecule of hydrogen fluoride (the mass of the molecular ion formed connections: 345, and the starting material - 365). Dedicated compounds in the individual form in the NMRB ^{1}HB вЂ“B spectra contains an identical compounds (4a), a set of signals, characterized by double bond proton bicyclic structure (6,55B ppm

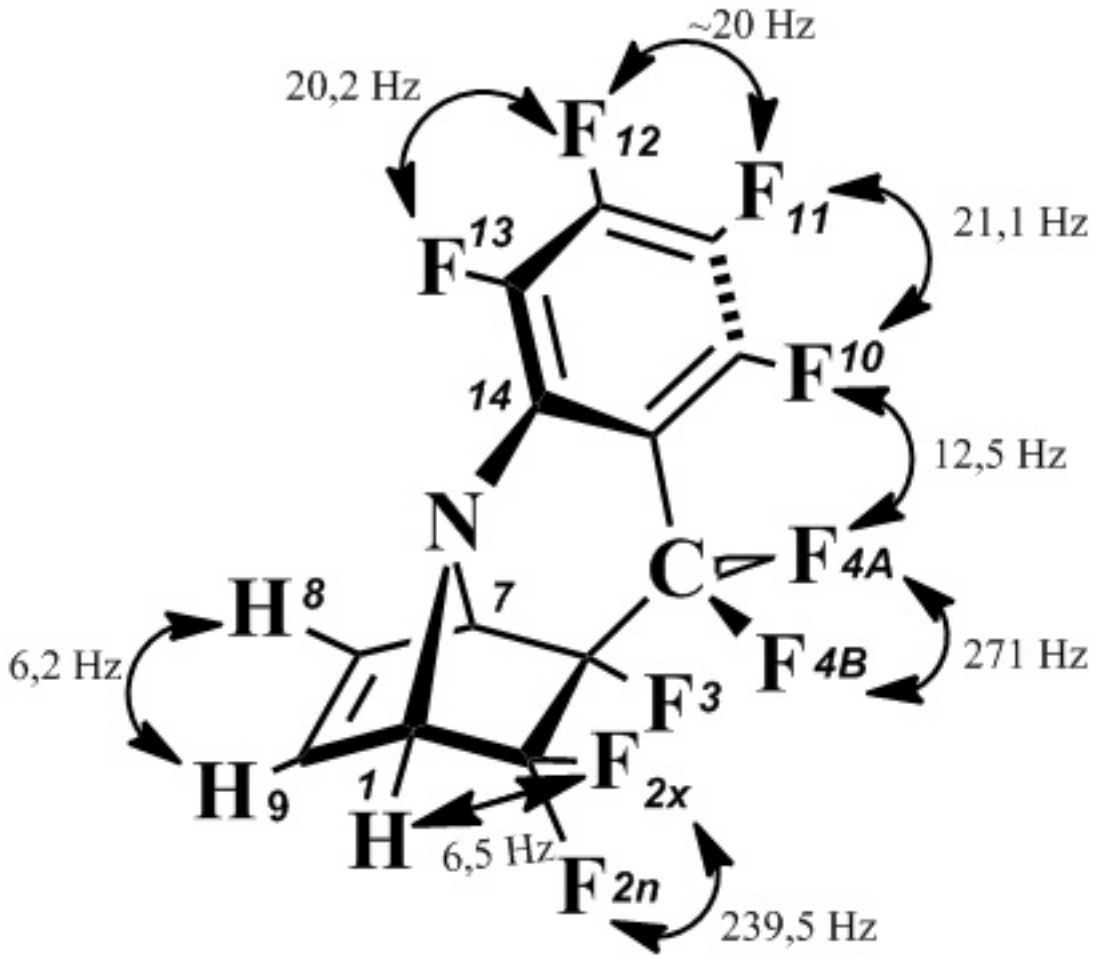
and 6,66B ppm) and вЂЊanchorвЂќ of protons (4,26B ppm and 4,48B ppm). COSY-spectrum also confirms the spin-spin interaction of the protons of the double bond and nodal protons. However, there is no a signal indicative of the nitrogen atom.

NMR spectra of ^{13}C and HSQC retained the same set of signals characteristic of the carbon structure of the compound (4a).

Thus, we can assume that when heated 6-exo-perfluorobenzyl-5,5,6-trifluoro-7-azabicyclo[2.2.1]hept-2-ene (4a) to 110-130B°C it is intramolecular cyclization with elimination of fluoride hydrogen to form tetracyclic compound (5).



NMR ^{19}F data also confirm the structure of the compound (5). Thus, the intensity of the signal corresponding to the fluorine atom in the ortho-position of the benzene ring is reduced by half, and the nature of the signals of the fluorine atoms in the meta-position is asymmetric:



However the formation of the adducts of fluorinated olefins adduct donвЂ™t occur directly to the nitrogen atom of the pyrrole.

Thus, it should be noted that the interaction of pyrrole with fluorinated olefins can both adducts accession in O±-position of the pyrrole ring and [2+4]-cycloaddition and вЂЊdominoвЂќ-reaction: adduct formation by reactions [2+4]-cycloaddition, followed by alkylation the resulting bicyclic secondary amine with perfluorobenzyl-group (for example, formation of compoud (5)).

Experimental

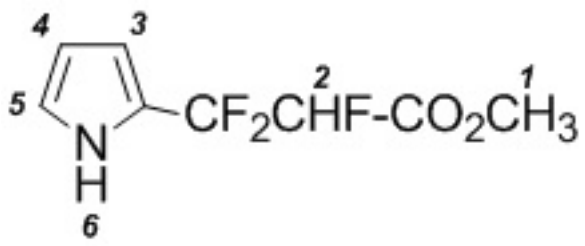
The structure of the synthesized compounds were confirmed by the data of the MS, NMR ^{1}H, ^{19}F, ^{13}C, HSQC and COSY-spectra.

NMR ^{1}H, ^{19}F, ^{13}C, HSQC and COSY were recorded with a Agilent DD2 NMR System 600 spectrometer (in DMSO-d_6 or $CDCl_3$) by temperature 25B°C on standard methods 1D and 2D experimentation. Chemical shifts are given in parts per million (ppm) relative to the tetramethylsilane (^{1}H, ^{13}C) and trifluoroacetic acid (^{19}F). The following abbreviations are used to describe peak patterns: s (singlet), d (doublet), dd (double doublet), tB (triplet), m (multiplet), q (quadruplet), and br (broad). Coupling constants are given in hertz.

Mass (m/z, relative intensity) spectra were recorded with detector HP-5975C at a voltage of 70 eV.

Methyl 2,3,3-trifluoro-3-(1H-pyrryl-2вЂ™)-propiolateB (1)

A solution 6,7B g (0,1B mol) pyrrole and 14,0B g (0,1B mol) methyl ester perfluoroacrylic acids in 100B ml dichloromethane was refluxed for 10B days. The solvent was evaporated, and the residue was purified by vacuum distillation. B.p. B 43B°C/20B mm.



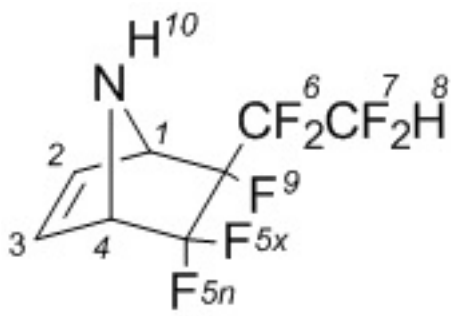
NMR ^{1}H ($CDCl_3$): 3,62B s (1-H, 3H); 6,11B m (4-H, 1H); 6,20B m (3-H, 1H); 6,74B m (5-H, 1H); 8,30B brB s (6-H, 1H).

MS, m/e (%): 207 (M^+,B 1); 187 ($[M\text{-}HF]^+$; 100); 155 ($[M\text{-}HF\text{-}OCH_3]^+$;36); 129 ($[M\text{-}HF\text{-}CO_2CH_3]^+$; 45).

5,5,6-Trifluoro-6-(2вЂ™-hydroperfluoroethyl)-7-azabicyclo-[2.2.1]hept-2-ens (2a Рё 2b)

A mixture of 4-hydroperfluorobut-1-ene (18,2B g; 0,10B mol) and pyrroles (30B g; 0,45B mol) was heated in steel autoclaves (150B ml) at 100B°C for 10B days. The autoclave was cooled until 0B°C. The reaction mixture has been distilled in vacuum. We received 6,4B g (0,026B mol; 26%) of colorless liquid with b.p.B 59-62B°C at 2B mm. The separation stereoisomeric mixture has been by flash chromatography on silica gel (cartridge 300g, spherical particles, sizeB -B 15Ojm, INTERCHIM) using dichloromethane as eluent. An analysis fractions has did by GC-chromatography. The first fraction contained 6B exo-(2вЂ™-hydroperfluoroethyl)-5,5,6-trifluoro-7-azabicyclo[2.2.1]hept-2-ene (2a) 1,8B g; followed by 6-endo-(2вЂ™-hydroperfuoroethyl)-5,5,6-trifluoro-7B azabicyclo[2.2.1]hept-2-ene (2b).

5,5,6-Trifluoro-6-exo-(2вЂ™B hydroperfluoroethyl)-7-azabicyclo-[2.2.1]hept-2-ene (2a)



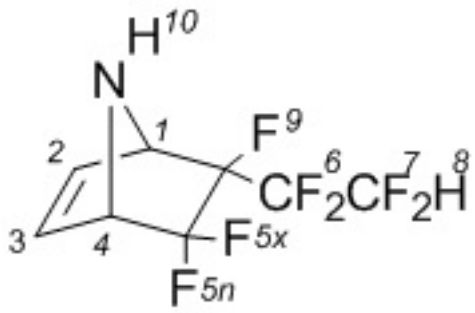
NMRB ^{1}H ($CDCl_3$): 2,31B brB s (10-H, 1H); 4,49B dB m (1-H, 1H); 4,37B m (4-H, 1H); 6,70B dm (2-H, 1H); 6,74B dm (3-H, 1H); 6,87B t (8-H, 1H).

NMRB ^{19}F ($CDCl_3$): -110,9B dB qB d (5x-F, $J_{5x\text{-}4}$=5,9 Hz; $J_{5xB\ 5n}$=228,9; 1F); B 104,71B d (5n-F, $J_{5x\text{-}5n}$=228,9; 1F); B 123,9B ddt (6_A-F; $J_{6\text{-}7}$=9,4B Hz; $J_{6AB\ 6B}$=277,7B Hz; 1F); B 124,2B dm (6_B-F; $J_{6AB\ 6B}$=277,7B Hz; 1F); B 135,1B dd (7_A-F; $J_{7\text{-}6}$=9,4B Hz; $J_{7AB\ 7B}$=299,3B Hz; 1F); B 137,3B ddm (7_B-F; $J_{7\text{-}6}$=9,4B Hz; $J_{7AB\ 7B}$=299,3B Hz; 1F); B 169,6B m (9-F, 1F).

NMR^{13}C ($CDCl_3$): 62,3 (1-C; 1C); 64,3 (4-C; 1C); 107,6 (C-F, 1C); 108,6 (C-F; 1C); 109,1 (C-F; 1C); 110,6 (C-F; 1C); 138,1 (3-C; 1C); 139,1 (2-C; 1C).

MS, m/e (%): 249 (M^+,B 1); 230 ($[M\text{-}F]^+$,B 2); 210 ($[M\text{-}2HF]^+$; 2); 198 ($[M\text{-}CF_2H]^+$; 6); 148 ($[M\text{-}C_2F_4H]^+$; 5); 67 ($[C_4H_5N]^+$; 100).

5,5,6-Trifluoro-6-endo-(2вЂ™-B hydroperfluoroethyl)-7-azabicyclo-[2.2.1]hept-2-ene (2b)



NMRB ^{1}H ($CDCl_3$): 2,81B brB s (10-H, 1H); 4,95B dm (1-H, 1H); 5,01B m (4-H, 1H); 6,67B dm (2-H, 1H); 6,74B dm (3-H, 1H); 6,59B t (8-H, 1H).

NMRB ^{19}F ($CDCl_3$): вЂ“108,7B dqd (5x-F, J_{5x-5n}=235,9B Hz, 1F); B 106,60B dq (5n-F, J_{5x-5n}=235,9B Hz, 1F); вЂ“122,0B d (6_A-F, J_{6A-6B}=289Hz, $J_{6B\ 7}$=8,1B Hz, 1F); вЂ“124,2B dm (6_B-F, J_{6A-6B}=289B Hz, J_{6-7}=8,1B Hz, 1F); B 137,52B ddm (7_A-F, J_{6-7}=8,1B Hz, J_{7A-7B}=305B Hz; J_{7-8}=51B Hz, 1F); B 139,3B ddm (7_B-F, J_{6-7}=8,1B Hz, J_{7A-7B}=305B Hz; J_{7-8}=51B Hz, 1F); вЂ“170,5B m.B (9B F, 1F).

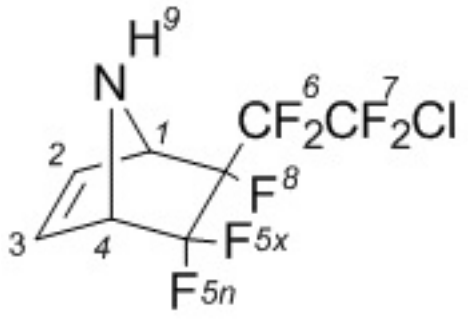
NMRB ^{13}C ($CDCl_3$): 62,8 (1-C; 1C); 64,3 (4-C; 1C); 107,6 (C-F, 1C); 108,7 (C-F; 1C); 109,1 (C-F; 1C); 110,6 (C-F; 1C); 133,5 (3-C; 1C); 134,0 (2-C; 1C).

MS, m/e (%): 230 ($[M-F]^+$,B 1); 210 ($[M-2HF]^+$; 1); 198 ($[M-CF_2H]^+$; 2); 148 ([MB $C_2F_4H]^+$, 5); 98 ($[C_5H_5FN]^+$, 9); 67 ($[C_4H_5N]^+$; 100).

5,5,6-Trifluoro-6-(2вЂ™-chloroperfluoroethyl)-7-azabicyclo-[2.2.1]hept-2-enes (3a and 3b)

A mixture of 4-chloroheptafluorobut-1-ene (30,0B g; 0,14B mol) and pyrroles (29,1B g; 0,43B mol) was heated in steel autoclaves (150B ml) at 100B°C for 10B days. The autoclave was cooled until 0B°C. The reaction mixture has been distilled in vacuum. Has been received 7,1B g 5,5,6-trifluoro-6-(2вЂ™-chloroperfluoroethyl)-7-azabicyclo[2.2.1]hept-2-ene of colorless liquid with b.p.B 72-74B°C at 1,5B mm. The separation stereoisomeric mixture has been by flash chromatography on silica gel (cartridge 300g, spherical particles, sizeB -B 15Ojm, INTERCHIM) using dichloromethane as eluent. An analysis fractions has did by GC-chromatography. The first fraction contained 5,5,6-trifluoro-6-exo-(2вЂ™-hydroperfluoroethyl)-7-azabicyclo[2.2.1]hept-2-ene (3a) 4,92B g; followed by 6-endo-(2вЂ™-hydroperfuoroethyl)-5,5,6-trifluoro-7-azabicyclo[2.2.1]-hept-2-ene (3b) 9,27B g.

5,5,6-Trifluoro-exo-6-(2'-chloroperfluoroethyl)-7-azabicyclo-[2.2.1]hept-2-ene (3a)



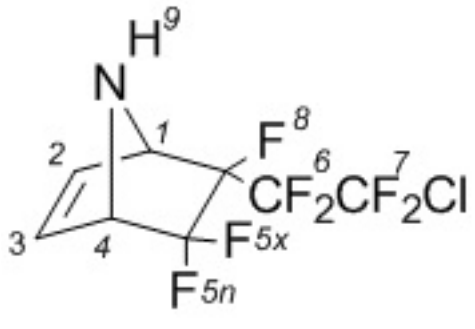
NMRB ^{1}H ($CDCl_3$): 2,3B brB s (9-H, 1H); 4,2B dm (4-H, 1H); 4,6B m (1-H, 1H); 6,6B dm (2-H; J_{2-3}=5,5B Hz; 1H); 6,6B dm (3-H; J_{3-2}=5,5B Hz; 1H).

NMRB ^{19}F ($CDCl_3$): B 110,2B dm (5x-F, J_{5x-4}=6B Hz; J_{5x-5n}=237B Hz; 1F); B 105,9B d (5n-F, J_{5x-5n}=237B Hz; 1F); B 112,2B dm (6_A-F; $J_{6AB\ 6B}$=289B Hz; 1F); B 114,4B ddm (6_B-F; $J_{6AB\ 6B}$=289B Hz; 1F); B 64,8B dm (7_A-F; $J_{7AB\ 7B}$=178B Hz; 1F); B 65,6B dt (7_B-F; J_{7B-6B}=21B Hz; $J_{7AB\ 7B}$=178B Hz; 1F); B 164,41B m (8-F, 1F).

NMRB ^{13}C ($CDCl_3$): 65,8 (4-C; 1C); 66,6 (1-C; 1C); 125,95 (C-F, 1C); 123,8 (C-F; 1C); 114,4 (C-F; 1C); 111,8 (C-F; 1C); 135,2 (2-C; 1C); 136,7 (3-C; 1C).

MS, m/e (%): 283 (M^+,B 1); 264 ($[M-F]^+$,B 1); 248 ($[M-Cl]^+$; 1); 198 ($[M-CF_2Cl]^+$; 23); 148 ($[M-C_2F_4Cl]^+$; 9); 67 ($[C_4H_5N]^+$; 100)

5,5,6-Trifluoro-endo-6-(2'-chloroperfluoroethyl)-7-azabicyclo-[2.2.1]hept-2-ene (3b)



NMRB ^{1}H ($CDCl_3$): 2,83 brB s (9-H, 1H); 4,09B dm (4-H, 1H); 4,32B m (1-H, 1H); 6,42B dm (2-H; J_{2-3}=4,8B Hz; 1H); 6,52B dm (3-H; J_{3-2}=4,8B Hz; 1H).

NMRB ^{19}F ($CDCl_3$): вЂ“109,7B dd (5x-F, J_{5x-5n}=232B Hz, 1F); B 105,6B dq (5n-F, J_{5x-5n}=232B Hz, 1F); вЂ“111,8B dd (6_A-F, J_{6A-6B}=288B Hz, J_{6A-7A}=17B Hz, 1F); вЂ“114,99B ddm (6_B-F, J_{6A-6B}=288B Hz, J_{6B-7B}=23B Hz, 1F); B 66,7B dm (7_AB F, $J_{7AB\ 7B}$=179B Hz; 1F); B 67,4B ddm (7_B-F, J_{6B-7B}=23B Hz, J_{7A-7B}=179B Hz); B 168,9B mB (8B F, 1F).

NMRB ^{13}C ($CDCl_3$): 64,2 (4-C; 1C); 66,1 (1-C; 1C); 111,6 (C-F, 1C); 113,3 (C-F; 1C); 123,7 (C-F; 1C); 125,5 (C-F; 1C); 134,0 (2-C; 1C); 135,0 (3-C; 1C).

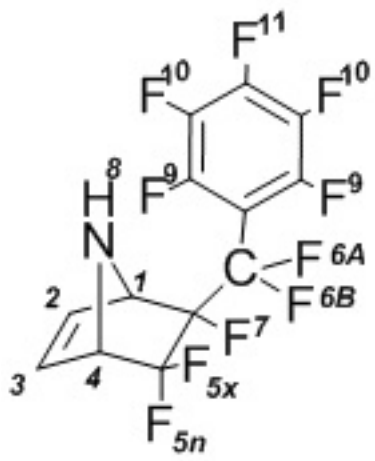
MS, m/e (%): 264 ($[M-F]^+$,B 1); 248 ($[M-Cl]^+$; 1); 198 ($[M-CF_2Cl]^+$; 20); 148 ($[M-C_2F_4Cl]^+$; 22); 67 ($[C_4H_5N]^+$; 100).

5,5,6-Trifluoro-6-perfluorobenzyl-7-azabicyclo[2.2.1]hept-2-enes (4a and 4b)

A mixture of perfluoroallylbenzene (29,8B g; 0,1B mol) and pyrroles (6,7B g; 0,1B mol) was heated at 100-110B°C under argon for 5B days.

The resulting mixture was cooled to room temperature. Unreacted ferfluoroallylbenzene and pyrrole has evaporated at 1B mm (room temperature). The residue was purified by flash chromatography on silica gel (cartridge 800g, spherical particles, sizeB -B 15Ojm, INTERCHIM) using chloroform as eluent. An analysis fractions has did by GC-chromatography. The first fraction contained 4,78B g 6-exo-perfluorobenzyl-5,5,6-trifluoro-6-perfluorobenzyl-7-azabicyclo[2.2.1]hept-2-ene (4a), followed by 9,27B g 5,5,6-trifluoro-6-endo-perfluorobenzyl-7B azabicyclo[2.2.1]-hept-2-ene (4b).

5,5,6-Trifluoro-6-exo-perfluorobenzyl-7-azabicyclo[2.2.1]hept-2-ene (4a); mp 55B°C.



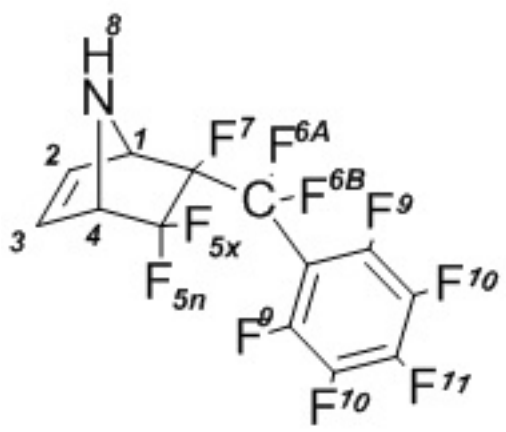
NMRB ^{1}H ($CDCl_3$): 2,53B brB s (8-H, 1H); 4,16B dm (4-H, J_{4-5x} = 5,1B Hz, 1H); 4,49B dm (1-H, 1H); 6,57B dm (2-H, J_{2-3} = 4,5B Hz, 1H); 6,62B dm (3-H, J_{2-3} = 4,5B Hz, 1H).

NMRB ^{19}F ($CDCl_3$): вЂ“113,4B dm (5x-F, 1F); вЂ“104B d (5n-F, 1F); вЂ“99,2B dt (6A-F, 1F); B 100,4B dm (6B-F, 1F); вЂ“170,0B dq (7-F, 1F); вЂ“160,3B t (9-F, 2F); вЂ“136,5B dm (10-F, 2F); вЂ“148,5B t (11-F, 1F).

NMRB ^{13}C ($CDCl_3$): 62,4B d (C^1H, JB =B 22B Hz); 64,4B t (C^4H, JB =B 24B Hz); 116,9B d (CF); 118,6B d (CF); 120,2B d (CF); 121,9B d (CF); 123,7B d (CF); 135,5 (CH=CH).

MS, m/e (%): 365 (M^+,B 1); 346 ($[M-F]^+$,B 2); 298 ($[C_9F_{10}]^+$, 2); 279 ($[C_9F_9]^+$, 5); 248B ($[C_8F_8]^+$; 3); 217B ($[C_7F_7]^+$; 19); 167B ($[C_6F_5]^+$; 4); 67 ($[C_4H_5N]^+$; 100).

5,5,6-Trifluoro-6-endo-perfluorobenzyl-7-azabicyclo[2.2.1]hept-2-ene (4b); mp 74B°C.



NMRB ^{1}H ($CDCl_3$): 2,82B brB s (8-H, 1H); 4,07B dm (4-H, J_{4-5x} = 5,4B Hz, 1H); 4,12B dm (1-H, 1H); 6,56B dm (2-H, 1H); 6,59B dm (3-H, 1H).

NMRB ^{19}F ($CDCl_3$): вЂ“110,1B dd (5x-F, 1F); вЂ“106,2B d (5n-F, 1F); B 101,8B ddq (6A-F, 1F); вЂ“95,8B dt (6B-F, 1F); вЂ“163,96B m (7-F, 1F); B 159,9B t (9-F, 2F); вЂ“137,4B dm (10-F, 2F); вЂ“148,1B t (11-F, 1F).

NMRB ^{13}C ($CDCl_3$): 64,7B d (C^1H, JB =B 25B Hz); 65,7B d (C^4H, JB =B 23B Hz); 122,3B d (CF); 124,1B d (CF); 125,9B d (CF); 135,5B d (CF); 135,5 (CH=CH), 136,8 (CH=CH).

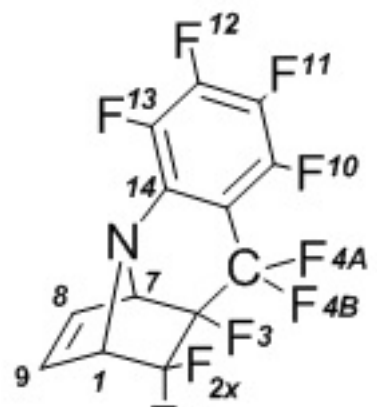
MS, m/e (%): 365 (M^+,B 1); 346 ($[M-F]^+$,B 3); 298 ($[C_9F_{10}]^+$;2); 279 ($[C_9F_9]^+$; 6); 248B ($[C_8F_8]^+$; 4); 217B ($[C_7F_7]^+$; 21); 167B ($[C_6F_5]^+$; 4); 67 ($[C_4H_5N]^+$; 100). $^+$

Perfluorobenz[1,2-e]-2,2,3-trifluoro-6-azatricyclo-[4.3.0.$0^{3,7}$]nonen-8 (5)

A mixture of perfluoroallylbenzene (29,8B g; 0,1B mol) and pyrroles (6,7B g; 0,1B mol) was heated at 120-135B°C under argon for 12B days.

The resulting mixture was cooled to room temperature. Unreacted ferfluoroallylbenzene and pyrrole has evaporated at 1B mm (room temperature). The residue was purified by flash chromatography on silica gel (cartridge 800g, spherical particles, sizeB -B 15Ojm, INTERCHIM) using chloroform as eluent. An analysis fractions were made by GC-chromatography. The first fraction contained 10,8B g perfluorobenz[1,2-e]-2,2,3-trifluoro-6-azatricyclo[4.3.0.$0^{3,7}$]nonena-8, followed by 0,77B g 6-exo-perfluorobenzyl-5,5,6-trifluoro-6-perfluorobenzyl-7-azabicyclo[2.2.1]-hept-2-ene (4a) and 9,27B g 5,5,6-trifluoro-6-endo-perfluorobenzyl-7-azabicyclo[2.2.1]-hept-2-ene (4b).

Perfluorobenz[1,2-e]-2,2,3-trifluoro-6-azatricyclo[4.3.0.$0^{3,7}$]-nonene-8 (6); mp 53B°C.



NMRB ^1H ($CDCl_3$): 4,25B dm (1-H, $J_{1\text{-}2x}$ = 6,5B Hz, 1H); 4,48B m (7-H, 1H); 6,55B dd (8-H, $J_{8\text{-}9}$ = 6,2B Hz, $J_{7\text{-}8}$ = 2,6B Hz, 1H); 6,67B dd (9-H, $J_{9\text{-}1}$ = 6,2B Hz; $J_{9\text{-}8}$ = 6,2B Hz; 1H).

NMRB ^{19}F ($CDCl_3$): вЂ“97,6B dd (4_A-F, $J_{4A\text{-}4B}$=271B Hz; $J_{10B\ 4A}$=13B Hz; 1F); B 99,8B dt (2_X-F, $J_{2C\ldots\text{-}2n}$=240B Hz; $J_{2x\text{-}1}$=7B Hz; 1F); B 107,7B dd (2n-F, $J_{2C\ldots B\ 2n}$=240B Hz; J=30B Hz; 1F); B 120,1B dqd (4_B-F, $J_{4A\text{-}4B}$=271B Hz; J=12B Hz; 1F); вЂ“139,7B m (11-F, $J_{11\text{-}10}$=21B Hz; 1F); вЂ“148,0B dd (10-F, $J_{10B\ 11}$=21,1B Hz; $J_{10B\ 4A}$=12,5B Hz; 1F); B 148,7B t (12-F; $J_{12\text{-}13}$=20B Hz; 1F); B 155,1B t (13-F, $J_{13B\ 12}$=20B Hz; 1F); вЂ“197,6B m (3-F, 1F).

NMRB ^{13}C ($CDCl_3$): 67,5 (C-7); 70,1 (C-1); 114,2B (C_{sp3}-F); 123,4B (C_{sp3}-F); 128,7 (C_{sp3}-F); 131,5 (C-8); 134,1 (C-9); 139,1B Pґ (C_{sp2}-F); 144,2B (C_{sp2}-F); 146,0 (C_{sp2}-F).

MS, m/e (%): 345 (M^+,B 26); 326 ($[M-F]^+$,B 31); 276 ($[M-CF_3]^+$;100); 226B ($[M-C_2F_5]^+$; 21).

References

1. I.Yu., Alexeev A.N., Benda A.F., Study pyrrols in reaction with olefines. 5th Youth Scientific School-conference of Organic Chemistry 22-26 april 2002, Ekaterinburg, p.73.
2. Jones R.A., Bean G.P. The Chemistry of Pyrroles. A series of monographs: ORGANIC CHEMISTRY, v. 34. Academic Press. 1977, p. 146.
3. Trebs A., Michl K.-H. Anlagerung von AcrylsГ¤ure und ihren Derivaten an Pyrrole. Annalen der Chemie. B.B 589, 1954, p.B 163-173.
4. Fischer H., Loewe H. Гњber die Anlagerung von Acrylnitril an Pyrrole. Annalen der Chemie. B.B 615, 1958, p.B 124-136.
5. Gonzalez J., Koontz J.I., Hodges L.M., et. al. Osmium-Promoted Dipolal Cycloadditions with Pyrroles: An Efficient, Stereoselective Synthesis of 7-Azanorbornanes. J.B Am. Chem. Soc., 1995, v. 117, pp. 3405- 3421.

Recommended for publication by Prof. A. F. Eleev

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