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Reactions of quadricyclane with fluorinated nitrogen-containing compounds. Synthesis of 3-aza-4-perfluoroalkyl-tricyclo [4.2.1.0^{2,5}]non-3,7-dienes

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Abstract

The cycloaddition reactions of quadricyclane (**1**) and polyfluorinated imines and nitriles were studied. Both $(CF_3)_2C{=}NH$ and $(CF_3)_2C{=}N$–(2-F–C_6H_4) were found to have low reactivity towards **1**, giving the corresponding [2 + 2 + 2] cycloadducts in a low yield. $C_2F_5N{=}CFCF_3$ however, reacts with **1** rapidly, giving a mixture of two isomeric cycloadducts in a high yield. Perfluoroalkyl nitriles R_fCN ($R_f = CF_3$, C_2F_5, *n*-C_3F_7) were found to have surprisingly high reactivity to **1** producing *exo*-3-aza-4-(fluoroalkyl)-tricyclo[4.2.1.0^{2,5}]non-3,7-dienes in 56–81% yields at elevated temperature. *Exo*-3-aza-4-(perfluoroalkyl)-tricyclo[4.2.1.0^{2,5}]non-3,7-dienes rapidly react with $CF_3Si(CH_3)_3$ in the presence of CsF catalyst. The reaction results in addition of $CF_3Si(CH_3)_3$ across the C=N bond of the azadienes with selective formation of only one stereoisomer of *exo*-3-aza-3-(trimethylsilyl)-4,4-bis(perfluoroalkyl)-tricyclo[4.2.1.0^{2,5}]non-7-enes. Silyl group in this compounds can be removed either by the action of tetrabutylammonium fluoride hydrate, leading to the formation of the corresponding amine after hydrolysis, or by reaction with HCl resulting in the formation of the corresponding amine hydrochloride.

Keywords: Quadricyclane; Imine of hexafluoroacetone; Perfluoro-3-azapentene-2; Trifluoroacetonitrile; Pentafluoropropionitrile; Perfluorobutyronitrile; Trifluoromethyltrimethylsilane

1. Introduction

The unique reactivity of saturated strained hydrocarbon—tetracyclo[3.2.0.0.^{2,7}.0^{4,6}]heptane (quadricyclane, **1**)—has been of considerable experimental and theoretical interest to organic chemists in the last 40 years [1]. Despite the fact that numerous examples of [$2_\sigma + 2_\sigma + 2_\pi$] cycloaddition reactions of **1** with a variety of dienophiles [2–11] have been reported, data on the reactions of **1** with nitrogen-containing compounds are limited to a few examples including cycloaddition of **1** to R–N=N–R [5,6], bis(phenylsulfonyl)-*o*-benzoquinondiimine [11], $RN{=}CHP(O)(OEt)_2$ [10] and several fluorinated azines [7–9]. Most of reported [2 + 2 + 2] reactions of **1** are quite interesting from the point of view of synthetic chemistry, since due to high stereoselectivity these reactions often result in selective formation of *exo*-tricyclononene derivatives, containing a four-membered fragment in *exo*-position relative to one carbon bridge of the norbornene system [1,5–11]. In search for new monomers for preparation of functional polymers for the next generation microlithography [12,13], we started investigation of the reactivity of quadricyclane towards fluorinated substrates. Recently, we have demonstrated that fluorinated carbonyl compounds rapidly react with **1** with the formation of a variety of norbonenoxetanes [14]. In this study an investigation of the reactivity of nitrogen-containing substrates towards **1** was attempted.

2. Results and discussion

In sharp contrast to hexafluoroacetone, which reacts with **1** exothermally [14], the reaction of imine of hexaflu-

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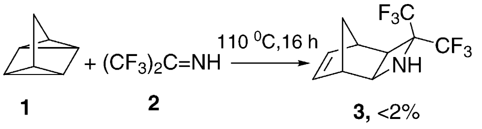
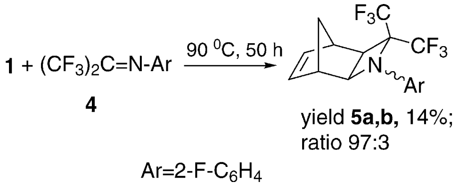
oroacetone (**2**) with **1** is very slow even at elevated temperature (110 °C, 16 h) leading to formation of trace of the cycloadduct **3**.



(1)

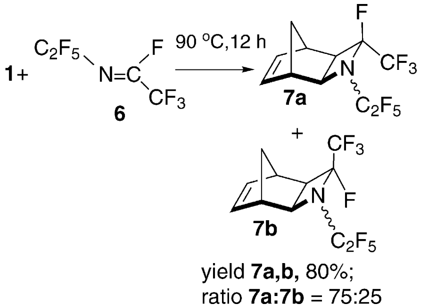
N-(2-Fluorophenyl)imine of hexafluoroacetone (**4**) in reaction with **1** showed slightly higher reactivity, giving cycloadduct **5** in low yield after prolonged heating of the reaction mixture [15].



(2)

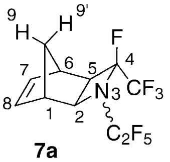
Detailed analysis of the isolated product by NMR spectroscopy revealed the presence of a small amount (~3%) of second isomer **5b**. Formation of isomers in this reaction is the result of *syn*- versus *anti*- orientation of aryl group at nitrogen relative to the methylene bridge of the norbornene fragment and it is indicative of relatively high barrier of nitrogen inversion in **5a**,**b**. Although unequivocal assignment structures of **5a**,**b** has not been attempted in this work, it is reasonable to postulate on steric grounds that major isomer has the substituent at nitrogen in *anti*-position to the norbornene methylene bridge.

anti-Perfluoro-3-azapentene-2 (**6**) [16,17] is significantly more reactive towards **1**. The reaction rapidly proceeds in a closed system (100 °C, 12 h, a significant pressure drop was observed in first 2 h of the reaction) with the formation of two isomers of *exo*-3-aza-3-pentafluoroethyl-4-trifluoromethyl-4-fluorotricyclo[4.2.1.$0^{2,5}$]non-7-ene (**7a**,**b**).

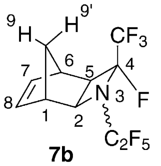


(3)

Based on NMR data the ratio of two isomers **7a**,**b** in isolated product is 75:25. The ^{1}H NMR spectrum of mixture **7a**,**b** exhibit two sets of signals, containing seven resonances for each isomer with relative intensities 1:1:1:2:1:1:1. Two signals of vinyl protons at ~6 ppm are indicative of presence of the double bond in the norbornene fragment. In major isomer (**7a**, see structure below) H-2 (δ = 3.48, dd, J = 14.7, 4.9 Hz) is coupled to H-5 (δ = 2.31, ddt, J = 6.3, 4.9, 1.0 Hz).



7a

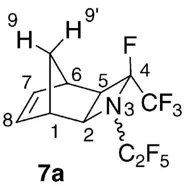


7b

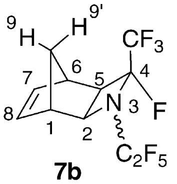
The value of coupling constant $J^3_{\text{H-2–H-5}} = 4.9$ Hz is indicative of *cis*-orientation of these two protons and is in a good agreement with *exo*-orientation of azacyclobutane ring [1]. In minor isomer **7b** the value of coupling constant H-2/H-5 is slightly higher ($J^3_{\text{H-2–H-5}} = 5.7$ Hz). It should be pointed out that stereoselective formation of *exo*-3-aza-tricyclo[4.2.1.$0^{2,5}$]non-7-enes was also previously reported in the reactions of fluorinated azines and **1** [7–9].

The formation of two isomers in the reaction of **1** and **6** is probably, the result of different orientation of substituents at C-4 relative to the methylene bridge of norbornene system. It is reasonable to believe that in major isomer (**7a**) smaller substituent, fluorine, is in *syn*- and the bulkiest substituent, CF_3 group is in *anti*-position relative to the norbornene methylene bridge. The stereochemistry of **7a** and **7b** was confirmed by data of 2D ^{1}H–^{19}F HOESY (Heteronuclear proton-fluorine 2D NOE) experiment carried out for mixture of isomers. Since in major isomer large NOE was observed between F-4 and H-9′ (CF_3-4 showed a large NOE to H-5 and a smaller NOE to H-2, see Fig. 1), major isomer indeed has structure **7a** with F-4 and H-9′ located in *syn*-position. Therefore, observed in ^{1}H, ^{19}F NMR spectra of **7a** four-bond coupling constant $J^4_{\text{H-2–F-4}} = 14.5$ Hz is "*trans*"-coupling constant between H-2 and F-4, since two substituents are located on *different* sides of azacyclobutane ring. It should be pointed out, that similar coupling constant ($J^4_{\text{H-2–F-4}} = 12.5$ Hz) previously reported for major isomer of cycloadduct **1** and $CF_3CF{=}N{-}N{=}CFCF_3$ was interpreted as four-bond *cis*-coupling constant between hydrogen and fluorine [9], however, this statement was not supported by other spectroscopic evidences.

^{19}F NMR spectrum of minor isomer **7b** is distinctly different. First of all, substantial downfield shift is observed for resonance of F-4 (δ = −129.05 for **7b** versus δ = −141.70 for **7a**; similar downfield shift for F-4 was previously observed in ^{19}F NMR spectra of minor isomers of cycloadducts of **1** and $CF_3C(O)F$ or $FSO_2CF_2C(O)F$, also having *anti*-orientation of F-4 in an oxetane ring relative to CH_2 bridge [14]). In ^{1}H NMR spectrum of **7b** the signal of H-5 (δ = 2.22, dd, J = 21.5, 5.7 Hz), coupled to H-2 (δ = 3.87, d, J = 5.7 Hz) has also a substantial three-bond coupling constant to F-4 ($J^3_{\text{H-5–F-4}} = 21.5$ Hz). The confirmation of *syn*-orientation of CF_3-4 and H-9′ (*anti*-orientation of both H-5 and F-4, respectively) for minor isomer once again was obtained in 2D ^{1}H–^{19}F HOESY experiment, where large NOE's between H-9′/CF_3-4 and F-4/H-5 (and smaller NOE for F-4/H-2) were observed. So, the minor isomer has structure **7b** with H-2, H-5 and F-4 located on the *same* side



7a



7b

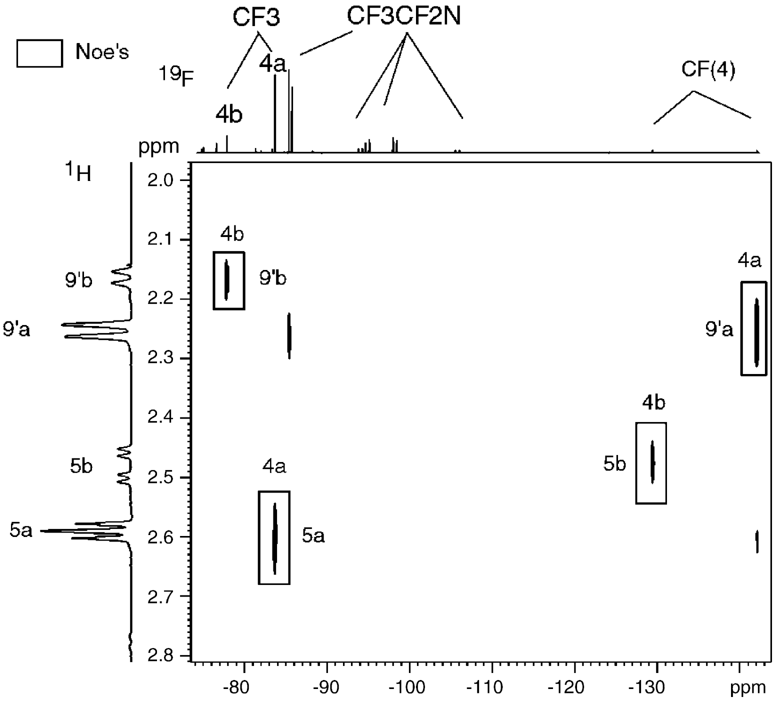
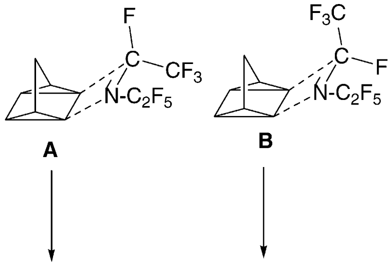


Fig. 1. Phase-sensitive 2D ^{19}F–^{1}H HOESY NMR expanded spectrum of a mixture of **7a** and **7b** isomers in dichloromethane-d$_2$ at 30 °C (only major NOE's are shown).

of azacyclobutane ring. Therefore, observed constant $J^3_{\text{H-5-F-4}} = 21.5$ Hz is *cis*-coupling constant between H-5 and F-4. Unusually high value of this constant probably results from combination of small dihedral angle F-4/C-4/C-5/H-5 and short distance between F-4 and H-5.

It should be pointed out, that NMR data however, were not sufficient to define the position N–CF$_2$CF$_3$ group in **7a** or **7b**. In HOESY experiment N–CF$_2$-group in both isomers **7a**,**b** showed small NOE to protons on *both* sides of norbornene fragment, indicating that nitrogen either is inverting rapidly on NMR time scale or is planar. The absence of major changes in ^{1}H and ^{19}F NMR spectra of **7a**,**b** at −70 °C in CD$_2$Cl$_2$ solvent (except for slight broadening of the signals of N–CF$_2$ group of major isomer) may be used as an argument in favor of planar nitrogen. However, at this point experimental data are not sufficient to exclude rapid nitrogen inversion process.

Assuming concerted mechanism of cycloaddition of **6** to **1**, the formation of isomers **7a**,**b** in this reaction can be explained as the result of different orientation of F and CF$_3$ substituents of **6** in transition state (**A** and **B**, Eq. 4) resulting in the formation of two isomers, **7a** and **7b**.

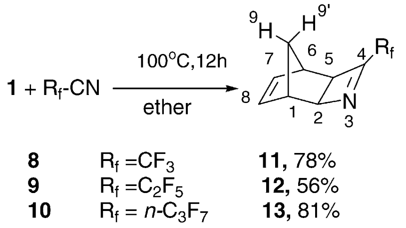


(4)

Transition state **A** (with F substituent of azaalkene **6** pointed towards CH$_2$ bridge of norbornene system) is responsible for the formation of major isomer **7a**. Less favorable, due to stronger steric interaction between bulkier CF$_3$ group and CH$_2$ bridge, transition state **B** leads to minor isomer **7b**. However, the formation of biradical intermediate in this reaction cannot be excluded either.

Nitriles, in general, are not active towards **1** and there are no reported examples of cycloaddition between **1** and nitriles [1]. In this study it was found that perfluorinated nitriles have surprisingly high reactivity towards **1**. In sharp contrast to acetonitrile, which is totally inert towards **1**

(100 °C, 16 h), CF_3CN (**8**) and nitriles **9**, **10** rapidly react with quadricyclane at elevated temperature producing *exo*-3-aza-4-perfluoroalkyltricyclo[4.2.1.$0^{2,5}$]non-3,7-dienes (**11–13**).



(5)

Despite the fact that cycloadducts of **1** with both acetylenes [1–3] and azocompounds [5,6] are known for over 30 years, the only reported representative of 3-azatricyclo[4.2.1.$0^{2,5}$]non-3,7-dienes is *endo*-3-aza-2,4,5-tris(*tert*-butyl)tricyclo[4.2.1.$0^{2,5}$]non-3,7-diene, prepared by reaction of tri-*tert*-butylazete and cyclopentadiene [18].

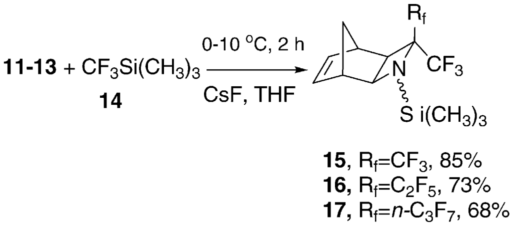
The activation of the nitrile functionality by strong electron-withdrawing group, such as perfluoroalkyl is essential, since no formation of the corresponding cycloadducts was observed in the reaction of **1** with either pentafluorobenzonitrile or acetonitrile under similar conditions. Observed order of reactivity on nitriles ($R_fCN \gg C_6F_5CN$, CH_3CN) correlates well with Hammet σ-constants for the corresponding substituents (σ_m/σ_p) CF_3: 0.43/0.54, C_2F_5: 0.47/0.52 versus C_6F_5: 0.26/0.27, CH_3: −0.07/−0.17 [19].

Isomer of **1**, norbornadiene, has quite different reactivity. In reaction with CF_3CN, which proceeds at higher temperature (180–190 °C) it was reported to give exclusively homo-Diels–Alder cycloadduct isolated in moderate yield (34%) after 40 h [20].

Azadienes **11–13** are colorless liquids, which can be isolated by vacuum distillation and stored at ambient temperature under inert atmosphere without decomposition for a long time. However, being exposed to air, these materials rapidly develop yellow-brown coloration, probably, due to oxidation. Air sensitivity and relatively high vapor pressure of materials (**11–13**) prevented obtaining satisfactory elemental analysis however, the proposed structures of **11–13** are in good agreement with data of IR, ^1H, ^{19}F, ^{13}C NMR, and mass spectroscopy. IR spectra of **11–13** exhibit weak absorption ~1600–1615 cm^{-1} assigned to C=N (cf. 1590 cm^{-1} for *endo*-3-aza-2,4,5-tris(*tert*-butyl)tricyclo[4.2.1.$0^{2,5}$]non-3,7-diene [18]). Each ^1H spectrum of compounds **11–13** containing eight well-separated signals of equal intensity, exhibits resonance of vinyl protons at 6.2–6.3 ppm (H-7, H-8, see Eq. (5)) having small but distinct difference in chemical shifts (~0.1 ppm); the value of coupling constants $J^3_{H\text{-}2-H\text{-}5}$ in **11–13** (determined in selective ^1H homodecoupling experiments) are smaller than similar coupling constant in **3**, **7a**,**b** [$J^3_{H\text{-}2-H\text{-}5} = 2.6$ for **11–13** versus 4.9 (**7a**) and 5.7 (**7b**) Hz; see Table 2] or **15–19**. Each {H} ^{13}C NMR spectrum of **11–13** along with other required resonances, exhibits two singlets at ~134 and ~137 ppm (C-7, C-8) and multiplet at ~180 ppm (C-4) coupled to α-fluorines of the corresponding perfluoroalkyl group (quartet, $J = 38$ Hz for **11** and triplets $J = 29$ and 30 Hz for **12**, **13**, respectively).

Mass spectra (EI) of **11–13** exhibit an $[M-1]^+$ peak of relatively high intensity. Fragmentation of the molecule involves loss of fluoroalkyl group with generation of $C_8H_8N^+$ ($m/z = 118$) ion transforming into $C_7H_7^+$ ($m/z = 91$), probably, through the extrusion of HCN.

The C=N bond in compounds **11–13** is highly reactive towards nucleophiles. For example, the reaction with $CF_3Si(CH_3)_3$ (**14**) in the presence of CsF catalyst proceeds exothermally in THF, giving products **15–17** in high yield.



(6)

According to NMR data (see Table 2), addition of $CF_3Si(CH_3)_3$ to compounds **11–13** is stereoselective, and leads to the formation of only one isomer in each reaction.

Silanes **15–17** are surprisingly stable to the action of dry CsF at ambient temperature. For example, no reaction was observed between **16** and CsF in THF (25 °C, 2 d, NMR).

Table 1
Ratio of reactants and reaction conditions

Entry no.	Reagents (mol)	Method	Temperature (°C)	Time (h)	Product (yield %)	Boiling point (°C/mmHg)	Analysis or MS[a]
1	**1** (0.21), **2** (0.25)	A	100	16	**3** (<2)		257 (M^+, $C_{10}H_9F_6N^+$)
2	**1** (0.05), **4** (0.01)	B	90	50	**5a**,**b** (14)	76–78/0.1	C, 54.41 (54.71); H, 3.34 (3.44); F, 37.30 (37.86)
3	**1** (0.2), **6** (0.18)	A	90	12	**7a**,**b** (80)	69–72/18	C, 40.68 (40.63); H, 2.61 (2.48); F, 52.47 (52.58)
4	**1** (0.34), **8** (0.25)	A	100	12	**11** (78)	54–55/13	181 [$(M-1)^+$, $C_9H_7F_3N^+$, 80], 118 [$(M-CF_3)^+$, $C_8H_8N^+$, 80], 91 ($C_7H_7^+$, 100)
5	**1** (0.3), **9** (0.17)	A	100	12	**12** (56)	63–64/15	236 [$(M-1)^+$, $C_{10}H_7F_5N^+$, 80], 118 [$(M-C_2F_5)^+$, $C_8H_8N^+$, 95], 91 ($C_7H_7^+$, 100)
6	**1** (0.2), **10** (0.15)	A	100	12	**13** (81)	72–73/13	236 [$(M-1)^+$, $C_{10}H_7F_5N^+$, 80], 118 [$(M-C_2F_5)^+$, $C_8H_8N^+$, 95], 91 ($C_7H_7^+$, 100)

[a] m/z, electronic ionization.

18, $R_f=CF_3$, 55%
19, $R_f=C_2F_5$, 45%

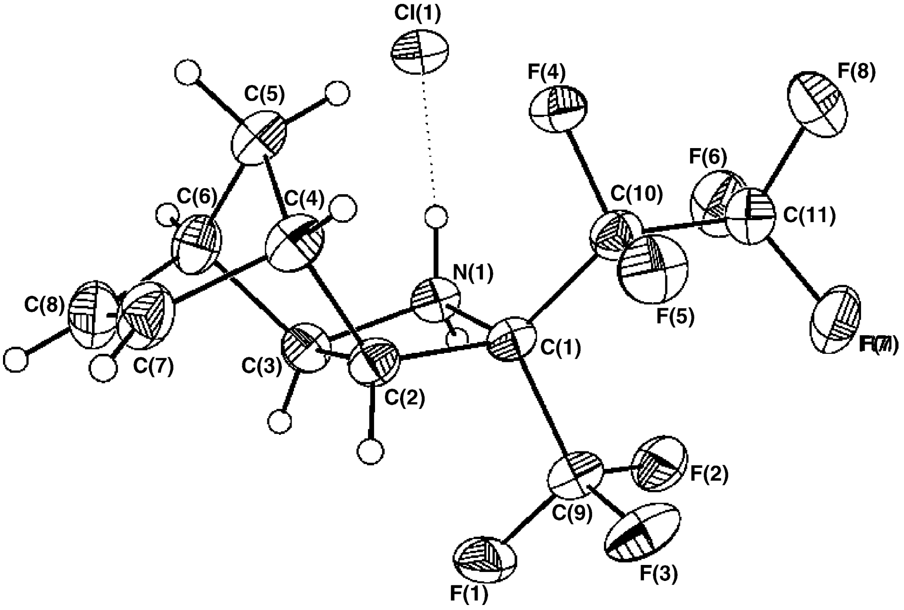
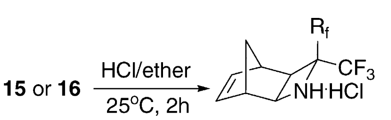


Fig. 2. ORTEP drawing of **19**. Thermal ellipsoids are drawn to the 50% probability level.

However, under the action of terabutylammonium fluoride hydrate compound **15** was converted into amine **3**.

$$\mathbf{15} \xrightarrow[\substack{\text{1) }(C_4H_9)_4NF\cdot\\ H_2O/THF\\ \text{2) }H^+}]{25\ ^\circ C,\ 2\ d} \mathbf{3} \quad \text{yield 90\%} \qquad (7)$$

The N–Si bond in **15–16** is sensitive to the action of acids. The reaction of **15** or **16** with a solution of hydrogen chloride in ether at ambient temperature results in rapid formation of the corresponding hydrochlorides **18** and **19**.



(8)

18, $R_f=CF_3$, 55%
19, $R_f=C_2F_5$, 45%

The structure of **19** was determined by single crystal X-ray diffraction. The nitrogen-containing cycle in **19** indeed has *exo*-geometry and pentafluoroethyl substituent pointed towards the CH_2 bridge (see Fig. 2). The molecules pack in hydrogen bonded pairs with two molecules and two chloride ions forming around a crystallographic center of symmetry.

The formation of **19** as a single isomer and *syn*-orientation of C_2F_5 group are both indicative of the addition of **14** to C=N bond occurring stereoselectively from the less hindered side of the molecule. Since only the C=N bond is involved in this reaction, it is reasonable to assume that precursor of **19** (compound **12**) also has *exo*-orientation of azabutane fragment and thus the addition of C_2F_5CN to **1** proceeds exclusively from *exo*-side.

The values of coupling constant between H-2/H-5, observed in ^1H NMR of compounds **3**, **15–19** ($J^3_{H\text{-}2-H\text{-}5} = 6.1$, 5.7, 5.5, 5.3, 6.1, 6.0 Hz, respectively; see Table 2) are typical for tricyclononene systems with *exo*-orientation of the four-member fragment [1,14]. It should be also emphasized that, the value of coupling constant $J^3_{H\text{-}2-H\text{-}5} = 6.0$ Hz observed in ^1H spectrum of **19** correlates well with the value of dihedral angle H–C(2)–C(5)–H (11.9°) obtained from X-ray diffraction experiment, since the value of H–H coupling constant is well known to be sensitive to dihedral angle, reaching the maximum value at 0° [21].

3. Conclusion

Reactivity of polyfluorinated imines and nitriles towards quadricyclane strongly depends on electron deficiency of carbon–nitrogen multiple bonds. Introduction of perfluoroalkyl groups into the molecule of imine or nitrile drastically increases the reactivity of fluorinated substrate towards **1**.

Addition of polyfluorinated imines and perfluoroalkylnitriles to **1** is stereoselective and leads to products with *exo*-orientation of the azacyclobutane (azacyclobutene) rings.

Based on isolated yields of products, the reactivity of the nitrogen-containing substrates studied decreases in the following order: $CF_3CF{=}NC_2F_5 \geq R_fCN > (CF_3)_2C{=}N{-}(2\text{-}F{-}C_6H_4) > (CF_3)_2C{=}NH$

Table 2
NMR and IR data for new compounds

Compound no.	^{1}H NMR[a] (δ, ppm, J, Hz)	^{19}F NMR[a] (δ, ppm, J, Hz)	^{13}C NMR[b] (δ, ppm, J, Hz)	IR[c] (cm^{-1})
3[d]	1.45(1H, d, 9.1), 2.35(1H, d, 6.1), 2.51(1H, d, 9.1), 2.60(1H, br s, NH), 2.88(1H, m), 3.10(1H, m), 3.77(1H, dm, 6.1), 5.95(1H, dd, 5.7, 3.0), 6.18(1H, dd, 5.7, 3.0)	−70.30(3F, q, 9.8), −77.47(3F, q, 9.8)	40.6, 41.7(m), 45.3, 58.9, 64.0(sept, 31), 123.6(q, 286.0), 125.4(q, 286.0), 134.2, 138.7	3372, 3311, 1459(w), 1370, 1318, 1259, 1138, 1100, 1014, 946, 803, 714
5a,b[e]	Major: 1.49(1H, d, 9.9), 2.38(2H, m), 3.18(1H, m), 3.25(1H, m), 4.28(1H, t, 3.9), 6.01(1H, dd), 6.25(1H, dd), 6.87(2H, m), 7.05(2H, m)	Major: −64.18(3F, hex. 9.0), −72.95(3F, dq, 9.0, 4.1), −128.55(1F, m)	–	–
	Minor: 1.59(1H, d, 10.0), 2.38(2H, m), 3.11(1H, m), 3.30(1H, m), 4.81(1H, d, 5.5), 6.01(1H, dd), 6.25(1H, dd), 6.87(2H, m), 7.49(2H, m)	Minor: −64.81(3F, hex. 9.0), −79.95, −133.93(1F, m)	–	–
7a[f]	1.55(1H, dm, 9.8), 1.95(1H, d, 9.8), 2.31(1H, dd, 6.3, 4.9, 1.0), 2.84(2H, s), 3.48(1H, dd, 14.7,[h] 4.9), 5.92(1H, dd, 5.7, 3.3), 6.19(1H, dd, 5.7, 3.0)	−83.15(3F, qq, 9.7, 1.7), −84.80(3F, s), −94.65(1F,d pent. 213.0, 10.4), −98.00(1F, d pent. 213.0, 10.4), −141.70(1F br.s, J_{d} = 14.7)[h]	–	1789(w), 1465(w)
7b[f]	1.35(1H, d), 1.80(1H, d, 9.8), 2.22(1H, dd, 21.5,[g] 5.7), 2.80(2H, s), 3.87(1H, d, 5.7), 5.93(1H, dd, 5.7, 3.0), 6.21(1H, dd, 5.7, 3.0)	−77.32(3F, dd, 14.3, 3.0), −85.15(3F, s), −93.75(1F, d pent., 215.0, 15.0), −105.60(1F, dqdd, 215.0, 14.3, 6.7, 1.0), −129.05(1F br.t, J_{t} ∼18)[g]		
11	1.28(1H, d, 10.5), 1.53(1H, d, 10.5), 2.70(1H, oct., J = 1.3, 2.6[h] Hz), 2.92(1H, s), 3.00(1H), 3.82(1H, d oct., J = 1.3, 2.6[h] Hz), 6.20(1H, dd, 3.2, 5.2), 6.28(1H, dd, 3.2, 5.2)	−73.81(d, 2.0)	36.7, 39.8, 40.1, 47.7, 66.4, 118.4(q, 276.0), 134.5, 137.0, 180.0(q, 38.0)	2978, 1615(w), 1460(w), 1366(s), 1180, 1140, 1080, 939, 707(s)
12	1.34(1H, d, 10.3), 1.63(1H, d pent., 10.3, 1.2), 2.80(1H, sept., J = 1.3, 2.6[h] Hz), 3.22(1H, m), 3.75(1H, d sept., J = 1.3, 2.6[h] Hz), 6.28(1H, dd, 5.5, 3.2), 6.35(1H, dd, 5.5, 3.0)	−83.40(3F, t, 2.5), −112.30(1F, dm, 272.0), −122.70 (1F, dm, 272.0)	36.7, 39.4, 39.8, 48.3, 67.1, 108.3(tq, 212.0, 39.0), 118.5(qt, 286.0, 35.0), 134.2, 136.7, 180.3(t, 29)	2978, 1605(w), 1565(w)
13	1.13(1H, d, 10.0), 1.42(1H, d pent., 10.0, 1.1), 2.58(1H, s), 2.75(1H, m), 2.83(1H, sept, J = 1.3, 2.6[h] Hz), 3.70(1H, sept., J = 1.3, 2.6[h] Hz), 6.08(1H, dd, 5.5, 3.2), 6.13(1H, dd, 5.5, 3.0)	−80.80(3F, t, 6.0), −120.00(1F, dqd, 297.0, 10.0, 2.0), −120.52(1F, dqd, 297.0, 10.0, 2.0), −127.22(1F, d, 294.0), −127.32(1Fd, 294.0)	36.8, 39.4, 39.8, 48.5, 67.0, 109.4(tm, 268.0, 39.0), 110.2(tt, 254.0, 33.0), 118.5(qt, 286.0, 33.0), 134.2, 136.7, 180.41(t, 30.0)	1460(w)
15	0.13(9H, s), 1.36(1H, d, 9.4), 2.22(1H, d, 5.7), 2.38(1H, d, 9.4), 2.91(1H, m), 3.05(1H, m), 3.59 (1H, d, 5.7), 5.89(1H, dd, 6.4, 3.4), 6.17(1H, dd, 6.4, 3.4)	−66.40(3F, q, 10.3), −70.03(3F, q, 10.3)		1456, 1409(w)
16	0.19(9H, s), 1.35(1H, d, 9.7), 2.35(1H, d, 5.5), 2.50(1H, d, 9.7), 2.95(1H, m), 3.05(1H, m), 3.69 (1H, d, 5.5), 5.91(1H, dd, 5.6, 3.4), 6.19(1H, dd, 5.6, 3.4)	−74.10(3F, qd, 10.3, 5.2), −80.10(3F, qd, 10.3), −112.20(1F, dq, 289.0, 5.2), −113.00(1F, dq, 289.0, 10.8)	−0.63, 41.02, 41.30(d, 15.5), 43.00, 46.09, 61.82, 67.50(m, 38.0), 114.11(tm, 263.0), 118.93(qt, 288.0, 35.0), 125.48(qd, 288.0, 9.7), 133.71, 138.60	1455, 1410(w)
17	0.16(9H, s), 1.35(1H, d, 9.5), 2.21(1H, d, 5.3), 2.47(1H, d m, 9.5), 2.95(1H, m), 2.99(1H, s), 3.71 (1H, d, 5.3), 5.91(1H, dd, 5.6, 3.1), 6.19(1H, dd, 5.6, 3.1)	−73.65(3F, m), −81.34(3F, dd, 15.6, 7.8), −109.50(2F, AB quart., 296.0), −124.00(2F, AB quart., 296.0)	−0.8, 41.00(d, 15.0), 41.36, 42.90, 46.00, 62.01, 68.12(m, 29.0), 110.11(tq, 271.0, 38.0), 115.90(tm, 262.0, 38.0), 118.00(qt, 289.0, 35.0), 125.30(qd, 288.0, 10.0), 133.61, 138.64	1455, 1411(w)

18	1.83(1H, d, 11.3), 2.64(1H, dd, 11.3, 6.1), 3.10(2H, s), 3.30(1H, s), 4.22 (1H, d, 6.1), 6.25(1H, dd, 5.3, 2.9), 6.33(1H, 5.3, 2.9), 7.50(2H, br. s)	−66.59(3F, br. s), −74.43(3F, br. q, 10.6)	–	–
19	1.55(1H, d, 11), 2.43(1H, d, 6.0), 2.62(1H, d, 11), 3.25(1H, s), 3.30(1H, d), 4.10 (1H, d, 6.0), 5.93(1H, dd, 5.6, 3.3), 6.19(1H, dd, 5.6, 3.3), 8.0 (2H, br. s)	−73.48(3F, br.s), −80.140(3F, q, 10.4), −112.20(1F, dq, 289.0, 5.2), −113.19(2F, AB quart. 289.0)	–	–

[a] In $CDCl_3$ as a solvent.

[b] Neat, {H} ^{13}C.

[c] Liquid film, KCl plates.

[d] Small amount of material, which can possibly be a second isomer of **3** was detected in crude product derived from the reaction of **1** and **2,** however, this isomer was not characterized due to low concentration; the presence of second isomer was not detected in compound **3** prepared by basic hydrolysis of **15** (NMR).

[e] Mixture of isomers, ratio 97:3.

[f] Mixture of isomers, ratio 75:25.

[g] Value of coupling constant was obtained in ^{19}F {H} experiment.

[h] Value of coupling constant was obtained in ^{1}H selective homodecoupling experiment.

4. Experimental

^{1}H and ^{19}F NMR spectra were recorded on a Brucker DRX-400 (400.5524 and 376.8485 MHz, respectively) instruments using $CFCl_3$ as an internal standard and $CDCl_3$ as a lock solvent. ^{1}H COSY experiments for compounds **11–13** were carried out in a Brucker DRX-500 (499.8731 MHz). The 2D ^{1}H–^{19}F HOESY (^{19}F observed) spectrum [22] of **7a**,**b** was obtained on a 500 MHz Bruker Avance DRX spectrometer, where ^{19}F appears at 470.712 MHz in CD_2Cl_2 solvent. The pulse sequence use was Hoesyph found in their pulse sequence library. The spectrum was obtained at 30 °C using a 500 ms mixing time, 10 s recycle time (due to the long relaxation times of the fluorine), 2048 t_2 points, 64 scan averages, and 128 t_1 with a 51282.051 Hz t_2 and a 3369.59 Hz t_1 spectral width and with ^{1}H decoupling during the acquisitions time. The spectrum was processed using a Gaussian function in t_2 with 2049 points and a Gaussian function in t_1 with 1024 points. The spectra are displayed in a phase-sensitive mode and linear prediction was used, backward in t_2 and forward in t_1 dimensions. IR spectra were recorded in a Perkin-Elmer 1600 FT spectrometer. Moisture sensitive materials were handled inside a glove box under inert atmosphere. GC and GC/MS analyses were carried out with an HP-6890 instrument using an HP FFAP capillary column and either a TCD (GC) or mass selective detector (GS/MS, EI), respectively. The crystal structure for **19** has been deposited at the Cambridge Crystallographic Data Center and allocated the deposition number CCDC 236156.

Compounds **8–10**, **14** (SyQuest), tetrabutylammonium fluoride hydrate (Aldrich) and other starting materials were purchased and used without further purification. Quadricyclane (**1**) was prepared by photochemical isomerization of norbornadiene [23] using *t*-butyl methyl ether as a solvent. For all reactions, material of a 90–95% purity was used [the remainder: norbornadiene (5–8%) and solvent (2–3%)]. Molar ratios of reagent are calculated based on pure **1** (Table 1). Compounds **2** [24], **4** [25] and **6** [16,17] were prepared according to the literature procedures.

4.1. Reactions of *1* with polyfluorinated nitrogen-containing compounds

4.1.1. Method A

Solution of 20–35 g (0.2–0.37 mol) of **1** in 100 mL of dry ether was placed in a 400 mL Hastelloy shaker tube. The reactor was cooled down, evacuated, charged with 20–42 g (0.17–0.27 mol) of fluorinated substrate and kept under autogenic pressure at 90–110 °C for 12–16 h. The reaction vessel was unloaded. The solvent was removed under a vacuum and the liquid residue was distilled under reduced pressure. Reaction conditions and ratio of reactants are given in Table 1.

4.1.2. Method B

A 20 mL glass sample vial was charged with a mixture of **1** (0.05–0.1 mol, 10–20% excess) and the corresponding substrate (0.03–0.08 mol), sealed and kept at 90–100 °C for a period of time indicated in Table 1. The product was isolated by vacuum distillation of the crude reaction mixture. Reaction conditions and ratio of reactants are given in Table 1.

4.2. Preparation of compound **15** (typical experiment)

To an agitated mixture of 50 mL of dry THF and 0.5 g (0.003 mol) of dry CsF was slowly added a mixture of 15 g (0.08 mol) of **11** and 12 g (0.084 mol) of **14** at 0–10 °C over a 40-min period. The reaction mixture was agitated for 30 min and poured in 400 mL of water. The mixture was extracted with CH_2Cl_2 (50 mL × 3), extract was washed with water (200 mL × 2), the solvent was removed under a vacuum and the residue was distilled under reduced pressure to give **15** (21 g, 85%), b.p. 56–57 °C/1 mmHg. MS (*m/e*): 329 (M^+, $C_{13}H_{17}F_6NSi^+$, 10%), 263($C_8H_{11}F_6NSi^+$, 100%). Compounds **16** and **17** were prepared similarly.

Compound **16**: yield 73%, b.p. 79–81 °C/2 mmHg. Anal. Calc. for $C_{14}H_{17}F_8NSi$: C, 44.32; H, 4.52, Found: C, 43.86; H, 4.41.

Compound **17**: yield 68%, b.p. 53 °C/0.3 mmHg. Anal. Calc. for $C_{15}H_{17}F_{10}NSi$: C, 41.96; H, 3.99; F, 44.25. Found: C, 41.73; H, 3.75; F, 44.31. Spectral data are given in Table 2.

Spectral data for **15–17** are given in Table 2.

4.3. Reaction of **15** with terabutylammonium fluoride hydrate

Five grams (0.015 mol) of **15** was dissolved in 30 mL of a 1 M solution of $(C_4H_9)_4N^+F^-/H_2O$ and the reaction mixture was agitated for 3 days at ambient temperature. It was poured in 400 mL of 10% hydrochloric acid, extracted with CH_2Cl_2 (20 mL × 2), the extract was washed with water (200 mL × 2), the solvent was removed under a vacuum and the residue was distilled under reduced pressure to give 3.2 g (85%) of **3**, b.p. 85–86 °C/30 mmHg. Anal. Calc. for $C_{10}H_9F_6N$: C, 46.70; H, 3.53; F, 44.32. Found: C, 46.42; H, 3.52; F, 44.10. Spectral data for **3** are given in Table 2.

4.4. Preparation of **18** and **19**

To 0.6 g of either **15** (or **16**) was added at ambient temperature 4 mL of 1 M solution of hydrogen chloride in ether. The reaction mixture was kept for 2–3 h at 25 °C, the precipitate formed was filtered, washed with a small amount of cold hexane and dried under a vacuum.

Compound **18**: yield 57%, m.p. 128–131 °C (dec.). Anal. Calc. for $C_{10}H_{10}ClF_{10}N$: C, 40.90; H, 3.43. Found: C, 40.72; H, 3.48. Spectral data for **3** are given in Table 2.

Compound **19**: yield 45%, m.p. 106–109 °C (dec.). Anal. Calc. for $C_{11}H_{10}ClF_8N$: C, 38.45; H, 2.93; F, 44.23. Found: C, 38.19; H, 2.89; F, 44.27. Spectral data for **3** are given in Table 2.

The sample of **19** for single crystal X-ray analysis was obtained by recrystallization of crude material from hexane.

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