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Dedicated to Academician of the Russian Academy of Sciences N.S.Zefirov on occasion of his70th anniversary

Fluoro-containing Heterocycles: XIV.* Cyclic Adducts of 6-Fluoro-7-azidoquinoxaline and Their Transformation Products

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Abstract—The possibility of a structural modification of quinoxalines through 1,3-dipolar cycloaddition of 7-azido-6-fluoroquinoxaline to norbornenes, enamines of cyclic ketones, and dimethyl acetylenedicarboxylate was demonstarated. The stability of 1,2,3-triazoline adducts was studied and the structure of the products of their molecular rearrangements was established. The cycloadduct of azide with cyclohexanone enamine undergoes azapinacolone rearrangement involving a contruction of the cycloalkane ring by one member affording amidine of cyclopentanecarboxylic acid. The triazoline adduct of the azide with dicyclopentadiene as a result of the rearrangement affords the corresponding aziridinoquinoxaline.

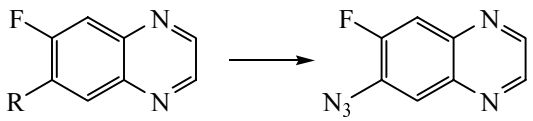
Quinoxalines are among the most important heterocycle classes [2–6], they are present in the composition of many biologically active substances, also of the naturally occurring compounds, in the complexing agents, luminophores, and other practically significant substances [2–9].

In extension of procedures for func-tionalization of fluoro-containing azaheterocycles we report here on the synthesis of 7-azido-6-fluoroquinoxaline and on the study of possible ways of quinoxaline structure modification by introducing fragments of various carbo- and heterocycles. Previously the synthesis of fluoroquinoxalines was performed by nucleophilic substitution of a fluorine in the benzene ring or by fusion of heterocycles to a pyrazine core [10, 11]. We describe here the use of the procedure of 1,3-dipolar cycloaddition for modification of fluoroquinoxalines via reactions of 7-azido-6-fluoroquinoxaline with alkenes and alkynes.

7-Azido-6-fluoroquinoxaline (**II**) was obtained from 6,7-difluoroquinoxaline (**Ia**) by reaction with sodium azide or by nitrosation of corresponding hydrazine derivative **Ib** (Scheme 1). Azide (**II**) was isolated in a crystalline state and characterized by elemental analysis, IR and ^{1}H NMR spectra. In the ^{1}H NMR spectrum of 7-azido-6-fluoroquinoxaline (**II**) the atoms H^5 and H^8 of the fluoroquinoxaline fragment give rise to two characteristic doublets at δ 8.04 ($^3J_{H,F}$ 11.7) and 8.01 ppm ($^4J_{H,F}$ 8.4 Hz).

Azide **II** is stable at storage, but sufficiently active in the reactions of 1,3-dipolar cycloaddition with norbornenes. Actually, azide **II** added to the double C=C bond of the norbornene (dioxane, 100°C, 2 h) affording *exo*-1,2,3-triazoline cycloadduct **III** whose structure was confirmed by the data of ^{1}H NMR and mass spectra (Scheme 2). In the ^{1}H NMR spectrum of compound **III** the signal from the nodal atom $H^{1'}$ appeared as a doublet at δ 4.76 ppm with ^3J 8.8 Hz. This value of the vicinal coupling constant (^3J ~9.0 Hz) is characteristic of the *exo*-junction of the triazoline and the bicycloheptane fragments [12]. We formerly showed that the product of cyclization of 7-azido-6-fluoroquinolone with norbornene, 1,2,3-triazoline cycloadduct, was a labile compound prone to a rearrangement into a 7-aminonorbornene through

Scheme 1.



Ia, Ib **II**

R = F (**a**), $NHNH_2$ (**b**).

* For communication XIII, see [1].

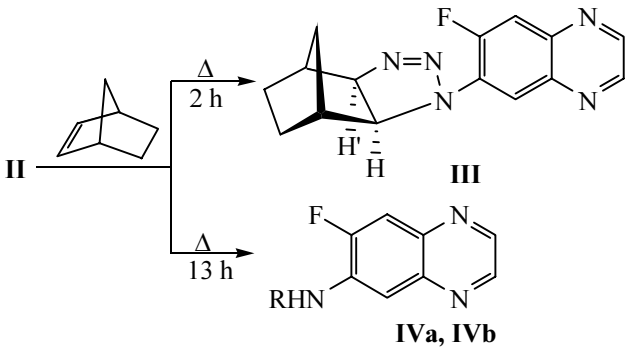
a nonclassical norbornyl cation [13]. We failed to find a product of a similar rearrangement in the reaction of 7-azido-6-fluoroquinoxaline with norbornene, and the prolonging the reaction time to 13 h resulted in the formation of 7-amino-6-fluoroquinoxaline (**IVa**).

At the cycloaddition of azide **II** to dicyclopentadiene a mixture of regioisomeric cycloadducts **Va** and **Vb** was obtained (Scheme 3, Fig. 1) which on heating in the aqueous ethanol lost a nitrogen molecule giving aziridine **VI**. After boiling in ethanol for 16 h the ^{1}H NMR spectrum contained only aziridine **VI** signals (Fig. 1) easily identified by the characteristic doublets from protons H^5 and H^8 at δ 7.60 ($^3J_{H,F}$ 11.2) and 7.45 ppm ($^4J_{H,F}$ 8.1 Hz).

The structure of aziridine **VI** was derived from the data of ^{1}H, ^{13}C, and 2D NMR spectra registered in COSY, NOESY, HSQC, and HMBC mode.*

In the aromatic region of the ^{13}C NMR spectrum appear eight signals from the carbon atoms of the substituted fluoroquinoxaline and two peaks from the carbons at the double C=C bond of the cyclopentene. The signals of the methylene and methine carbon atoms of the polycylic fragment at the C^7 atom of the fluoroquinoxaline were identified by the cross-peaks with the corresponding protons in the spectrum 2D HSQC,

Scheme 2.

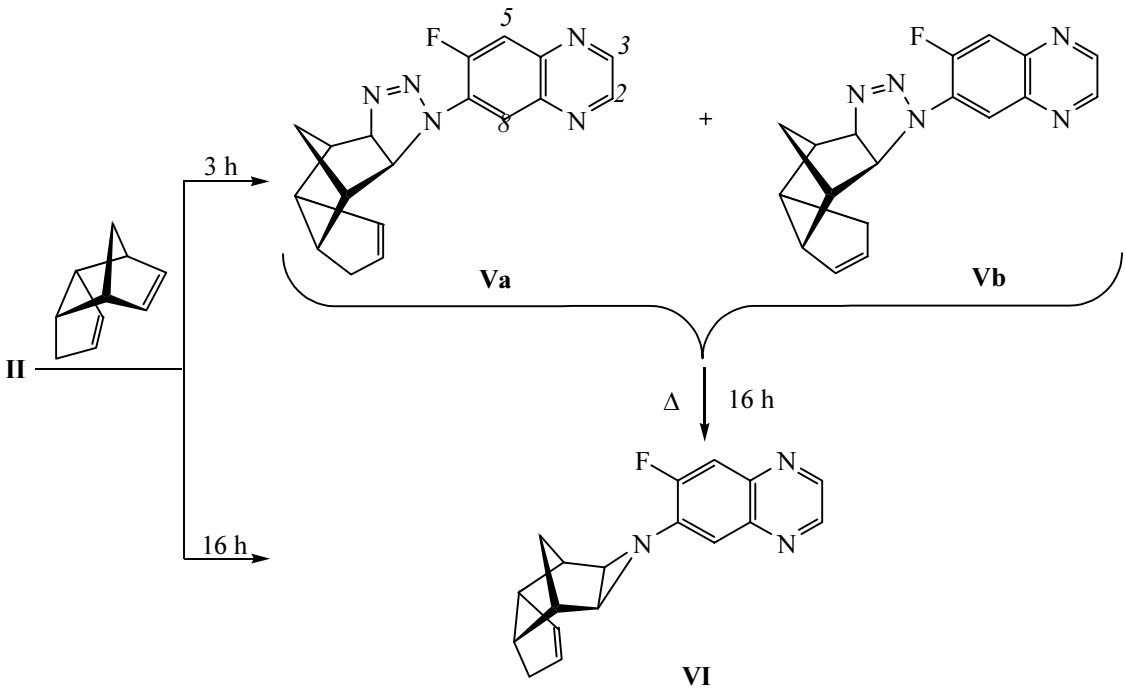


R = H (**a**), Ac (**b**).

and also basing on the couplings $^2J_{CH}$, $^3J_{CH}$ observed in the spectrum 2D HMBC. The signals of aziridine atoms $C^{8'}$ and $C^{10'}$ are located at 41.58 and 39.50 ppm, and the corresponding protons appear as doublets at 2.66 and 2.44 ppm respectively with a coupling constant 5.3 Hz.

The conclusion on the reciprocal spatial arrangement of the aziridine and cyclopentene rings with respect to the norbornane framework was based on the analysis of 2D NOESY spectra of compound **VI** (Fig. 2). The presence of cross-peaks due to the nuclear Overhauser effect between the proton $H^{11'b}$ and protons $H^{6'}$ and $H^{2'}$

Scheme 3.



*The authors are grateful to Dr.Chem.Sci. Yu.A. Strelenko for performing the NMR experiments.

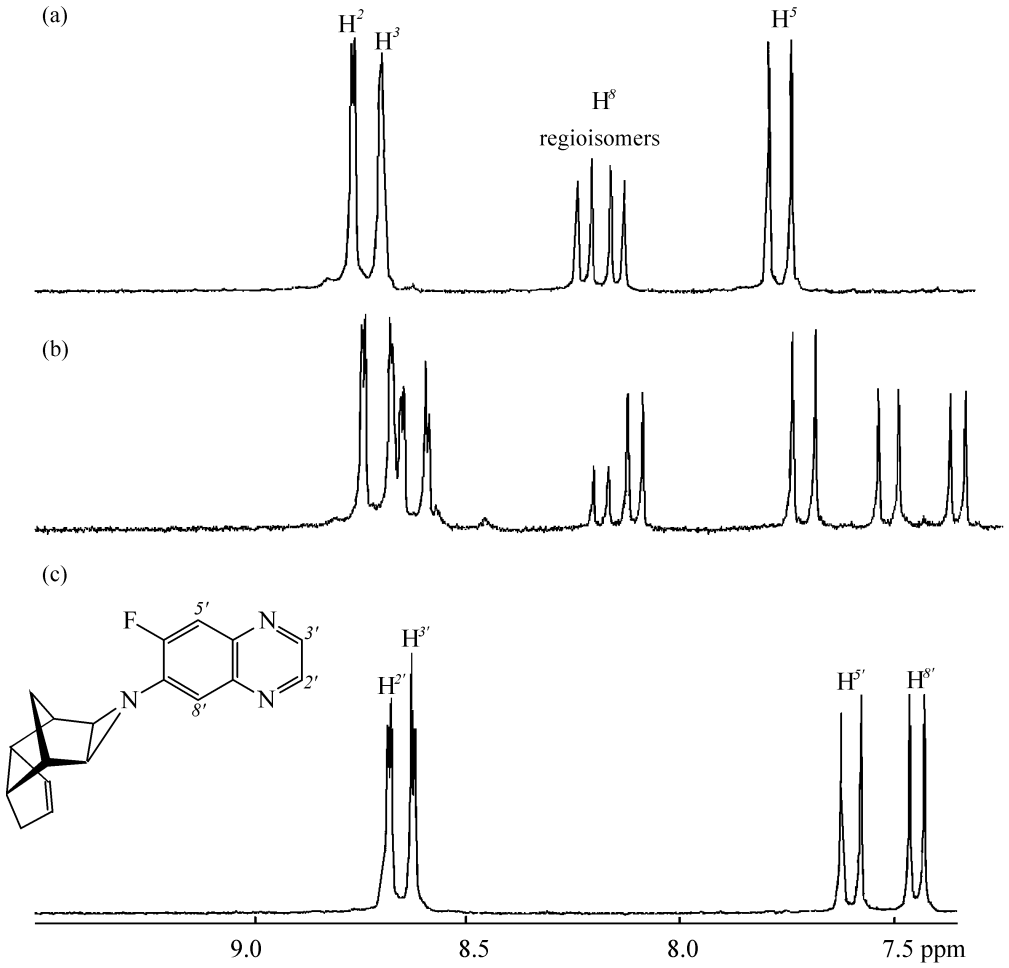


Fig. 1. Alterations in the ^{1}H NMR spectra in the course of conversion of triazolines **Va** and **Vb** into aziridine **VI**. (a) the spectrum of initial 1,2,3-triazolines **Va** and **Vb**; (b) the spectrum of a mixture of triazolines **Va** and **Vb** and aziridine **VI** after heating for 30 min; (c) the spectrum of aziridine **VI** after heating of triazolines **Va** and **Vb** for 16 h.

testifies to the *endo*-orientation of the cyclopentene fragment with respect to the norbornane. The existing cross-peaks between the cyclopentene protons (H$^{3'}$ and H$^{5'}$) and the nodal protons H$^{10'}$ and H$^{8'}$ respectively which in their turn correlate with each other (H$^{8'}$ and H$^{10'}$) indicate the *endo*-position of the nodal protons H$^{8'}$ and H$^{10'}$, and consequently the *exo*-orientation of the aziridine ring with respect to norbornane.

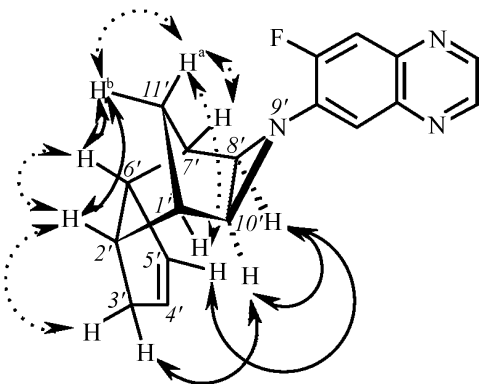
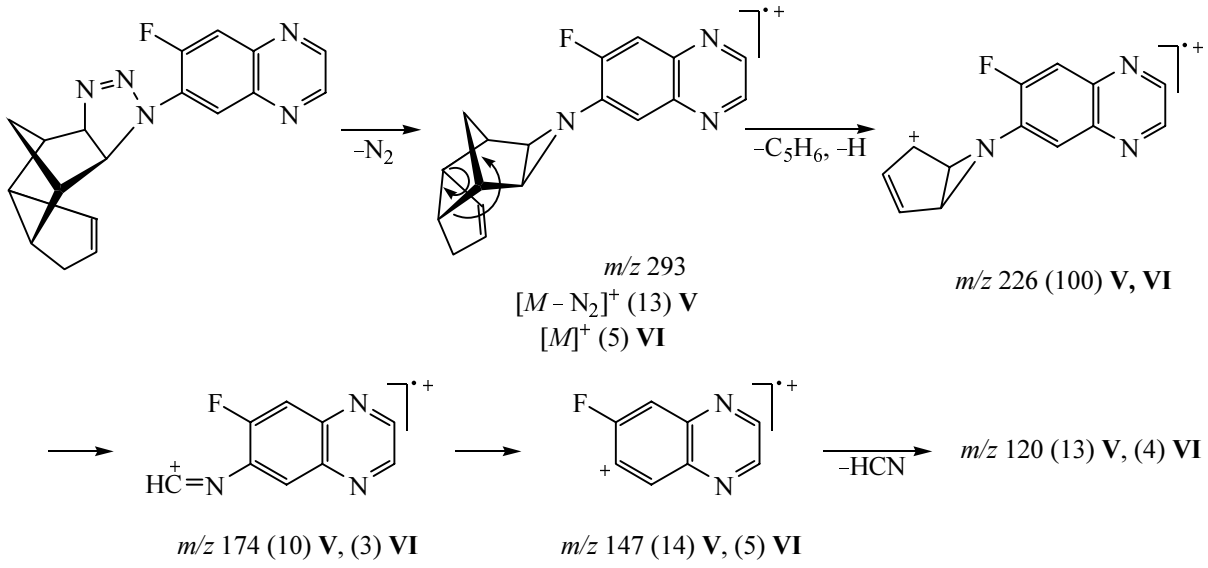


Fig. 2. Correlation in the spectra ^{1}H–^{1}H NOESY of aziridine **VI**.

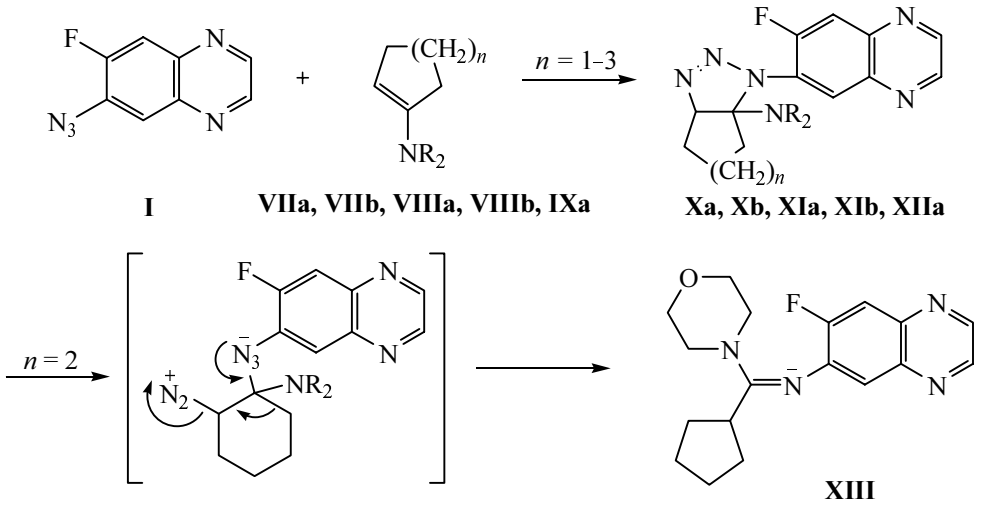
The correlation scheme obtained (Fig. 2) makes it possible to prove unambiguously the *endo*-orientation of the cyclopentene and *exo*-orientation of the aziridine rings with respect to the norbornane framework.

The process of rearrangement of triazolines **Va** and **Vb** into aziridine **VI** is conveniently followed by the signals of protons H^5 and H^8. The H^8 proton of triazolines **Va** and **Vb** gives rise to a signal in the region 8.16–8.23 ppm, and in aziridine **VI** it suffers an upfield shift (δ 7.45 ppm). The chemical shift of the signal from H^5 proton is less sensitive to the substituent at the C^7 atom: 7.78 in the spectrum of triazolines **Va** and **Vb**, and 7.60 ppm in that of aziridine **VI** (Fig. 1).

Scheme 4.



Scheme 5.



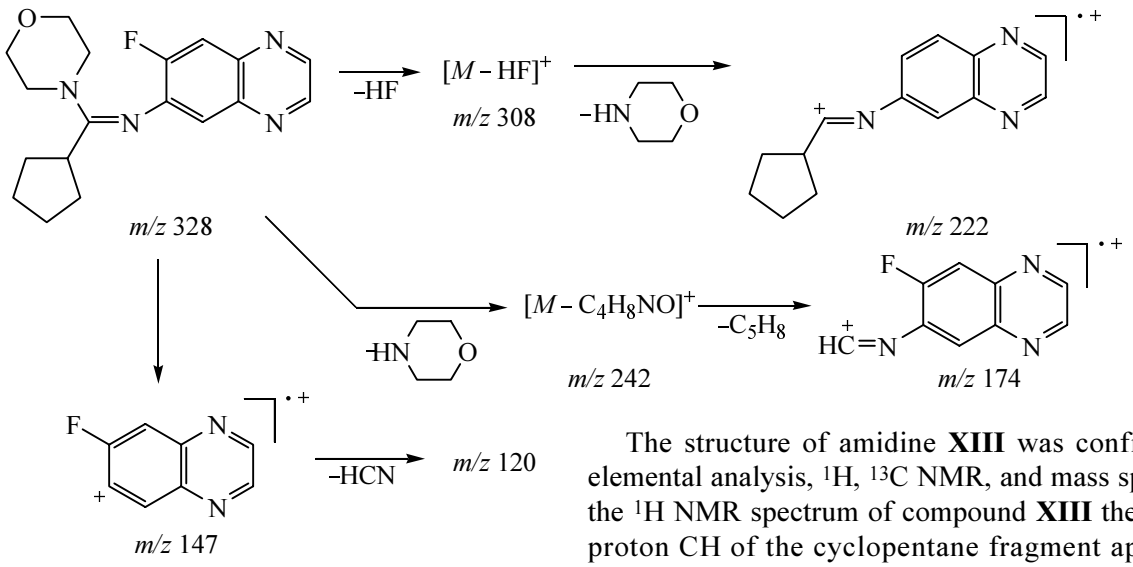
NR_2 = morpholino (**a**), piperidino (**b**); n = 1 (**VII, X**), 2 (**VIII, XI**), 3 (**IX, XII**).

In the mass spectra of the triazolines **Va** and **Vb** was registered a peak of pseudomolecular ion $[M-N_2]^+$ with *m/z* 293, and the paths of further fragmentations of triazolines **Va** and **Vb** are similar to those of aziridine **VI** (Scheme 4). Quite probably, the electron impact causes the rearrangement of triazolines **Va** and **Vb** into aziridine **VI**. The most abundant ion (100%) with *m/z* 226 forms by cleavage of the cyclopentadiene fragment C_5H_6 from the fragment ion $[M-N_2]^+$ in the case of triazolines **Va** and **Vb** or from $[M]^+$ in the case of aziridine **VI.**

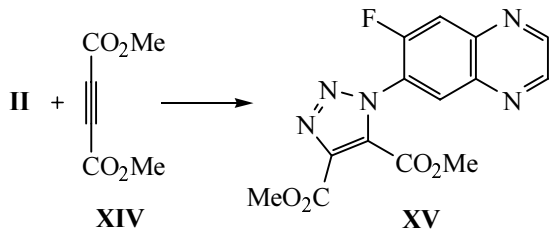
The behavior of azide **II** in reactions with norbornadiene is different. We failed to isolate individual cycloaddition products from the reaction mixture, but the NMR spectra showed that in several minutes from mixing the reagents formed at least three to four substances, and in 2.5 h a single component remained in the reaction mixture, namely 7-amino-6-fluoro-quinoxaline (**IV**).

The reaction of azide **II** with enamines of cyclic ketones **VII–IX** [14] occurred at room temperature and provided 1,2,3-triazoline adducts **Xa, Xb, XIa, XIb**, and **XIIa** (Scheme 5). The characteristic feature of the ^1H NMR spectra of triazolines **X–XII** is the position of the signal belonging to methine proton $H^{5'}$ that appears as a doublet of doublets at δ 4.70–4.86 ppm. Triazoline adducts **Xa, Xb, XIa, XIb**, and **XIIa** give in the mass

Scheme 6.



Scheme 7.



spectra a peak of the pseudomolecular ion $[M - N_2]^+$, and also eliminate enamine providing a peak of 7-amino-6-fluoroquinoxaline (I_{rel} 100%).

The regioorientation of addends in compounds **Xa, Xb, XIa, XIb**, and **XIIa** is consistent with the spectral data and with the common theoretical concepts on this type of cycloaddition which assume that the reaction should be controlled by the interaction between the LUMO of the electrophilic azide and HUMO of the electron-rich dipolarophile (enamine) and should result in formation 5-substituted 1,2,3-triazolines [15–17].

In the reaction of azide **II** with cyclohexanone enamine the primarily 1,2,3-triazoline cycloadduct **XI** readily eliminated a nitrogen molecule and suffered an azapinacolone rearrangement with a 1,2-alkyl shift resulting in amidine of cyclopentanecarboxylic acid **XIII**. The rearrangement scheme involving the intermediate formation of diazonium betaines, ejection of a nitrogen molecule, and 1,2-sigmatropic shift of an alkyl group was suggested based on the literature analogies [17, 18].

The structure of amidine **XIII** was confirmed by elemental analysis, ^1H, ^{13}C NMR, and mass spectra. In the ^1H NMR spectrum of compound **XIII** the methine proton CH of the cyclopentane fragment appears as a characteristic quintet at δ 2.94 ppm, and the corresponding carbon of the CH group gives a resonance in the ^{13}C NMR spectrum at 40.76 ppm; the carbon atoms of the methylene groups give rise to two signals at δ 26.08 and 30.27 ppm in accordance with their belonging to the symmetric cyclopentane moiety. The signal from the carbon atom of the amidine fragment in the ^{13}C NMR spectrum of compound **XIII** is observed as a singlet at 162.89 ppm.

In the mass spectrum of compound **XIII** the molecular ion peak was registered with *m/z* 328. The fragmentation pattern of M^+ supports the assumed structure (Scheme 6). The presence of a fluorine in the molecule predetermines HF elimination; the latter is possible only at the reciprocal *ortho*-position of these atoms (ion with *m/z* 308). Quinoxaline structure is detected by the ion with C *m/z* 147 $[C_8H_4FN_2]^+$ and by the secondary fragment ion with *m/z* 120. The presence of the morpholine ring is confirmed by the ion with *m/z* 242 arising at its elimination from M^+ , and by ion $[M - HF]^+$ with *m/z* 222. The strong peak with *m/z* 174 is formed from the fragment ion $[M - C_4H_8NO]^+$ by the rupture of a cyclopentane fragment C_5H_8.

1,3-Dipolar cycloaddition can be used also for introducing into the quinoxalines of a triazole fragment. It was established that the addition of azide **II** to dimethyl acetylenedicarboxylate in a boiling dioxane afforded 7-triazolyl-substituted 6-fluoroquinoxaline **XV** (Scheme 7).

In the electron-impact mass spectrum of quinoxaline **XV** was registered the molecular ion peak with *m/z* 331.

Here the 1,2,3-triazole ring did not eject a nitrogen molecule due to thermal reactions because the stability of the ring was ensured by aromaticity. The acetyl fragments elimination resulted in ions $[M - COOCH_3]^+$ with *m/z* 272 and $[M - 2COOCH_3]^+$ with *m/z* 213; further processes of the typical fragmentation of nitrogen-containing heterocycles with elimination of HCN provided ions with *m/z* 186 and 159.

It should be mentioned in conclusion that the reactions of 1,3-dipolar cycloaddition investigated in this work and the discovered transformations of the primary cycloadducts show the possibility of constructing new fluoroquinoxaline derivatives containing versatile heterocyclic fragments: triazolines, aziridines, amidines, and triazoles.

EXPERIMENTAL

^1H and ^{13}C NMR spectra were registered from solutions in DMSO-d_6 and $CDCl_3$ on spectrometers Bruker DRX-500, Bruker AM-300, Bruker WP-80-SY at operating frequencies 500.13, 300.13, and 80.13 MHz for protons, 125.76 MHz, and 75.43 MHz for ^{13}C. In the ^1H NMR spectra TMS was used as internal reference.

Mass spectra were measured on Varian MAT 311A instrument under the following conditions: accelerating voltage 3 kV, cathode emisson current 300 μA, ionizing electrons energy 70 eV, direct admission of the sample into the ion source.

7-Hydrazino-6-fluoroquinoxaline (I). To a dispersion of 3.0 g (6.0 mmol) of 6,7-difluoroquinoxaline (**II**) in 40 ml of ethanol was added 15 ml of hydrazine hydrate, and the mixture was heated at 80°C for 2 h. On cooling the separated precipitate was filtered off and recrystallized from aqueous ethanol, 1:1. Yield 2.3 g (71%), mp 187°C (decomp.). Found, %: C 54.01; H 3.94; N 31.30. $C_8H_7N_4F$. Calculated, %: C 53.93; H 3.96; N 31.45.

7-Azido-6-fluoroquinoxaline (II). *a.* To a dispersion of 2.4 g (13.5 mmol) of 7-hydrazino-6-fluoroquinoxaline (**Ib**) in 20 ml of 18% hydrochloric acid cooled to 0°C was added by portions a solution of 1.1 g of sodium nitrite in 11 ml of water maintaining the temperature below 0–3°C. The reaction mixture was kept on an ice bath for 1 h, the precipitate was filtered off and thoroughly washed with water. Yield 1.7 g (67%), mp 101–102°C (EtOH–H_2O). IR spectrum, cm^{-1}: 2105 [ν_{as} (N_3)]. Found, %: C 50.66; H 2.17; N 36.73. $C_8H_4FN_5$. Calculated, %: C 50.79; H 2.13; N 37.09.

b. A solution containing in 5 ml of DMF 1 g (6 mmol) of 6,7-difluoroquinoxaline and 1.3 g (19.6 mmol) of sodium azide was heated for 4 h at 100°C, then cooled, and poured into water. The separated precipitate was filtered off and recrystallized from aqueous ethanol, 1:1. Yield 752 mg (66%).

7-(3,4,5-Triazatricyclo[5,2,1^{1,7},0^{2,6}]deca-4-en-3-yl)-6-fluoroquinoxaline (III). A solution of 600 mg (3.17 mmol) of 7-azido-6-fluoroquinoxaline (**II**) and 597 mg (6.34 mmol) of norbornylene in 10 ml of dioxane was heated for 2 h at 100°C. The solvent was distilled off in a vacuum on a rotary evaporator, 2-propanol was added to the residue, the separated precipitate was filtered off, and recrystallized from hexane. Yield 386 mg (43%), mp 111–112°C. Found, %: C 63.66; H 4.98; N 24.77. $C_{14}H_{14}FN_5$. Calculated, %: C 63.59; H 4.98; N 24.72.

7-Amino-6-fluoroquinoxaline (IVa). A mixture of 737 mg (3.90 mmol) of 7-azido-6-fluoroquinoxaline (**II**) and 1.1 g (11.68 mmol) of norbornylene was heated for 13 h at 100°C. The solvent was distilled off in a vacuum on a rotary evaporator, ethyl ether was added to the residue, the separated precipitate was filtered off and dried in a vacuum. Yield 210 mg (33%).

To obtain plausible data of elemental analysis 7-acetylamino-6-fluoro-quinoxaline (**IVb**) was prepared.

7-Acetylamino-6-fluoroquinoxaline (IVb). A solution of 50 mg (0.31 mmol) of amine **IV** in 1.5 ml of acetic anhydride was heated for 0.5 h at 100°C. On diluting with 10 ml of water the solution was filtered, the solvent was distilled off in a vacuum on a rotary evaporator, 3 ml of cold water was added to the residue, the separated crystalline precipitate was filtered off. Yield 28 mg (45%), mp 203–204°C. Found, %: C 58.49; H 3.84; N 20.48. $C_8H_6FN_3$. Calculated, %: C 58.53; H 3.93; N 20.48.

7-(3,4,5-Triazatetracyclo[5.5.1.0^{2,6}0^{8,12}]trideca-4,9-dien-3-yl)-6-fluoroquinoxaline (V). A solution of 450 mg (2.38 mmol) of 7-azido-6-fluoroquinoxaline (**II**) and 629 mg (4.76 mmol) of dicyclopentadiene in 5 ml of dioxane was heated for 3 h at 90°C. The solvent was distilled off in a vacuum on a rotary evaporator, 2-propanol was added to the residue, the separated precipitate was filtered off and washed with ethyl ether. Yield 620 mg (68%), mp 140–142°C. Found, %: C 67.18; H 4.97; N 21.73. $C_{18}H_{16}FN_5$. Calculated, %: C 67.28; H 5.02; N 21.79. At attempt to recrystallization from the aqueous ethanol, 1:1, compound **V** partially transformed into aziridine **VI**.

7-(9-Azatetracyclo[5.3.1.0^{2,6}0^{8,10}]undec-4-en-9-yl)-6-fluoroquinoxaline (VI). (a) A solution of 0.6 g (3.17 mmol) of 7-azido-6-fluoroquinoxaline (**II**) and

1.05 g (3.18 mmol) of dicyclopentadiene in 10 ml of dioxane was heated for 16.5 h at 100°C. The solvent was distilled off in a vacuum on a rotary evaporator, 2-propanol was added to the residue, the separated precipitate was filtered off. Yield 300 mg (32%), mp 141–142°C.

b. A solution of 222 mg (3.90 mmol) of triazoline **V** in 10 ml of ethanol was heated at reflux for 16 h and then isolated as described in procedure *a.* Yield 68 mg (34%), mp 141–142°C. ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 31.40 s (C^{32}), 31.85 s (C^{112}), 38.01 s (C^{72}), 39.50 s (C^{102}), 39.55 s (C^{12}), 41.58 s (C^{82}), 41.82 s (C^{22}), 53.29 s (C^{62}), 112.60 d [C^5, ^2J(C^5, F^6) 18.9 Hz], 118.40 d [C^8, ^3J(C^8, F^6) 5.0 Hz], 129.84 s ($C^{5'}$), 132.33 s (C^{42}), 139.72 d [C^{4a}, ^3J(C^{4a}, F^6) 11.3 Hz], 141.20 s (C^{8a}), 142.89 s (C^3), 144.12 d [C^2, ^6J(C^2, F^6) 1.3 Hz], 145.85 d [C^7, ^2J(C^7, F^6) 15.1 Hz], 157.86 d [C^6, ^1J(C^6, F^6) 256.6 Hz]. Found, %: C 73.41; H 5.56; N 14.08. $C_{18}H_{16}FN_3$. Calculated, %: C 73.70; H 5.50; N 14.32.

7-(1-Morpholino-2,3,4-triazabicyclo[3.3.0]octen-3-yl)-6-fluoroquinoxaline (Xa). To a dispersion of 206 mg (1.09 mmol) of azide **II** in 5 ml of ethyl ether was added at stirring 334 mg (2.18 mmol) of 1-morpholino-1-cyclopentene. After stirring for 1 h at room temperature the precipitate was filtered off, washed with ethyl ether, and recrystallized from aqueous ethanol, 1:1. Yield 235 mg (63%), mp 132–133°C. Found, %: C 59.55; H 5.64; N 24.52. $C_{17}H_{19}FN_6O$. Calculated, %: C 59.64; H 5.59; N 24.55.

7-(1-Piperidino-2,3,4-triazabicyclo[3.3.0]octen-3-yl)-6-fluoroquinoxaline (Xb). To a dispersion of 326 mg (1.72 mmol) of azide **II** in 5 ml of 2-propanol was added at stirring 521 mg (3.44 mmol) of 1-piperidino-1-cyclopentene. After stirring for 1 h at room temperature the precipitate was filtered off, washed with ethyl ether, and recrystallized from aqueous ethanol, 1:1. Yield 445 mg (76%), mp 134–136°C. Found, %: C 63.58; H 6.14; N 24.59. $C_{18}H_{21}FN_6$. Calculated, %: C 63.51; H 6.22; N 24.69.

7-(1-Morpholino-2,3,4-triazabicyclo[4.3.0]-nonen-3-yl-2)-6-fluoroquinoxaline (XIa). To a dispersion of 150 mg (0.79 mmol) of azide **II** in 5 ml of ethyl ether was added at stirring 265 mg (1.59 mmol) 1-morpholino-1-cyclohexene. After stirring for 1 h at room temperature the precipitate was filtered off. Yield 70 mg (25%), mp 119–120°C. Found, %: C 60.82; H 6.0; N 23.79. $C_{18}H_{21}FN_6O$. Calculated, %: C 60.66; H 5.94; N 23.58.

At attempt to recrystallization compound **XIa** partially transformed into amidine **XIIIa**.

7-(1-Piperidino-2,3,4-triazabicyclo[4.3.0]-nonen-3-yl-2)-6-fluoroquinoxaline (XIb). To a dispersion of 200 mg (1.06 mmol) of azide **II** in 7 ml of ethyl ether was added at stirring 350 mg (2.11 mmol)of 1-piperidino-1-cyclohexene. After stirring for 3 h at room temperature the precipitate was filtered off. Yield 215 mg (57%), mp 112–113°C. Found, %: C 64.42; H 6.71; N 23.76. $C_{19}H_{23}FN_6$. Calculated, %: C 64.39; H 6.54; N 23.71.

7-(1-Morpholino-2,3,4-triazabicyclo[5.3.0]-decen-3-yl-2)-6-fluoroquinoxaline (XIIa). To a solution of 200 mg (1.06 mmol) of azide **II** in 2 ml of dioxane was added 0.4 g (2.1 mmol) of 1-morpholino-1-cycloheptene, and the mixture was left standing at room temperature for 4 h. The separated precipitate was filtered off, washed with ether, and recrystallized from 2-propanol. Yield 157 mg (40%), mp 158–160°C. Found, %: C 61.64; H 6.33; N 22.53. $C_{19}H_{23}FN_6O$. Calculated, %: C 61.60; H 6.26; N 22.69.

6-Fluoro-7-[morpholino(cyclopentyl)methylamino]quinoxaline (XIII). A dispersion of 1.0 g (3.62 mmol) of azide **II** and 1.21 g (7.30 mmol) of 1-morpholino-1-cyclohexene in 50 ml of dioxane was heated at reflux for 2 h. On cooling the separated precipitate was filtered off, recrystallized from aqueous ethanol, and dried in a vacuum over P_2O_5. Yield 333 mg (28%), mp 91–93°C. ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 26.08 s [2C, $(\underline{C}H_2)_2$], 30.27 s [2C, $(\underline{C}H_2)_2$], 40.76 s (1C, $\underline{C}H$ cyclopentene), 46.36 s [2C, $N(CH_2)_2$], 66.49 s [2C, $O(CH_2)_2$], 112.39 d [1C, C^5, ^2J(C^5, F^6) 21.1 Hz], 119.10 d [1C, C^8, ^3J(C^8, F^6) 3.3 Hz], 139.80 d [1C, C^{4a}, ^3J(C^{4a}, F^6) 12.3 Hz], 141.34 s (1C, C^{8a}), 142.58 s (1C, C^3), 143.86 d [1C, C^2, ^6J(C^2, F^6) 2.3 Hz], 143.87 d [1C, C^7, ^2J(C^7, F^6) 16.9 Hz], 156.55 d [1C, C^6, ^1J(C^6, F^6) 252.5 Hz], 162.89 s (1C, $\underline{C}$=N amidine). Found, %: C 65.80; H 6.52; N 16.83. $C_{18}H_{21}FN_4O$. Calculated, %: C 65.83; H 6.45; N 17.06.

7-[4,5-Bis(methoxycarbonyl)-1,2,3-triazol-1-yl]-6-fluoroquinoxaline (XV). To a solution of 1.0 g (5.29 mmol) of azide **II** in 15 ml of dioxane was added 0.9 ml (7.32 mmol) of dimethyl acetylenedicarboxylate, and the mixture was heated for 11 h at 100°C. The solvent was distilled off in a vacuum on a rotary evaporator, 2-propanol was added to the residue, the separated precipitate was filtered off and recrystallized from 2-propanol. Yield 718 mg (41%), mp 134–136°C (decomp.). Found, %: C 50.58; H 3.22; N 20.61. $C_{14}H_{10}FN_5O_4$. Calculated, %: C 50.76; H 3.04; N 21.14.

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