Chemistry of Heterocyclic Compounds **2020**, *56*(5), 537–541

Structural transformations of 2-(adamantan-1-yl)aziridines

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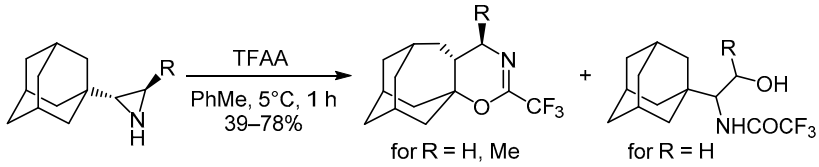
Translated from Khimiya Geterotsiklicheskikh Soedinenii, 2020, *56*(5), 537–541

Submitted January 14, 2020
Accepted after revision March 3, 2020



The specifics of transformations of sterically hindered 2-(adamantan-1-yl)aziridine derivatives in the presence of trifluoroacetic anhydride are considered. In a reaction with trifluoroacetic anhydride, *trans*-2-(adamantan-1-yl)-3-methylaziridine forms the rearrangement product dihydro-1,3-oxazine condensed with homoadamantane, whereas 2-(adamantan-1-yl)aziridine forms a mixture of a derivative of oxazine and *N*-[1-(adamantan-1-yl)-2-hydroxyethyl]-2,2,2-trifluoroacetamide in equal proportions.

Keywords: adamantane, aziridine, dihydro-1,3-oxazines, cage compounds, ring opening reactions, skeletal rearrangements.

Aziridine is an important building block in organic synthesis and is widely used to access various heterocyclic structures.[1–6] Many natural and synthetic compounds containing the aziridine fragment have a wide spectrum of biological activity and are used in antibacterial and anticancer therapy (Fig. 1).[4–8]

One of the important areas of aziridine chemistry is the ring expansion reactions leading to the formation of nitrogen-containing heterocycles, for example, pyrrolidines,[9] pyrrolidin-2-ones,[1] β-lactams,[1] imidazolines,[1] oxazolines,[10] thiazolidin-2-ones,[2] tetrahydro-1,3-oxazin-2-ones,[11] etc. Despite a significant number of reports of such chemical transformations, there is no information on the synthesis of dihydro-1,3-oxazines based on the opening of the aziridine ring. Moreover, it is known that derivatives of 1,3-oxazine are used as therapeutic agents with antimicrobial, antiviral, and antitumor effects (Fig. 2),[12–14] while 2*H*-1,3-benzoxazines are potassium channel regulators and have become candidate drugs for treatment of hypertension, angina pectoris, asthma, and other diseases.[15,16] It should be mentioned that 1,3-oxazines are also used in organic synthesis as starting compounds to access biologically more significant structures.[17–19]

Within the framework of this study, the transformations of aziridines containing a bulky substituent in their structure were examined. We believe that the presence of a conformationally rigid adamantane framework in the starting compound can affect both the reactivity of aziridine and the structure of the final product. The use of trifluoroacetic acid anhydride (TFAA) during the reaction makes it possible to incorporate the CF_3 group into the 1,3-oxazine ring and to obtain the previously unknown 2-(trifluoromethyl)dihydro-1,3-oxazines. Also, in the

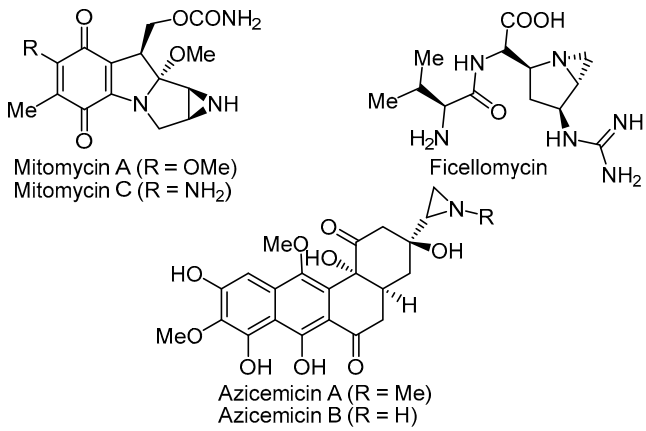


Figure 1. Medications containing the aziridine ring.

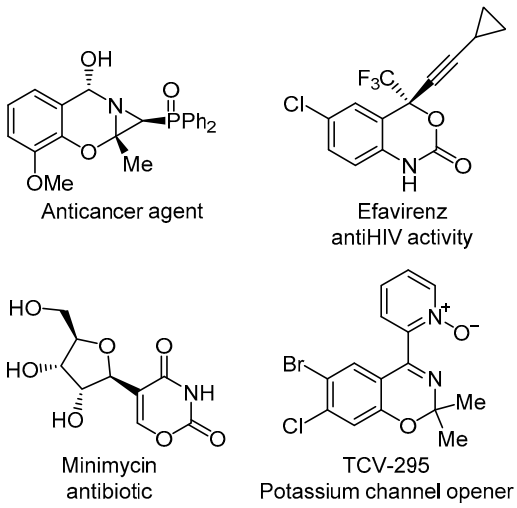


Figure 2. Structures of medicinal and biologically active compounds containing the oxazine ring.

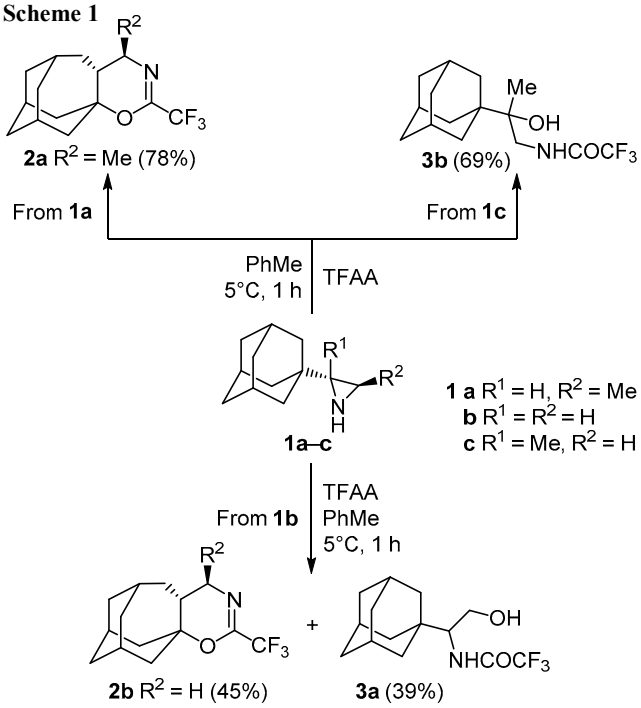
presence of TFAA the reaction proceeds *via* the formation of a carbocation and is accompanied by skeletal transformation of the adamantane framework due to the participation of electrons of σ-bonds.[20–24]

The starting aziridines **1a**–**c** were obtained by a known method[25] by reacting the corresponding adamantane olefins with NBS and NaN_3 followed by reduction of the resulting vicinal bromoazides. Next, an intramolecular rearrangement occurs upon the reaction of aziridines **1a**–**c** with TFAA in PhMe, which in the case of *trans*-2,3-disubstituted aziridine **1a** leads to the formation of 2-(trifluoromethyl)dihydro-1,3-oxazine **2a** condensed with homoadamantane in 78% yield (Scheme 1). In turn, the reaction of 2-(adamantan-1-yl)aziridine (**1b**) under similar conditions gives rise to a mixture of products, 2-(trifluoromethyl)dihydro-1,3-oxazine **2b** and amide **3a** in a 1:1 ratio. The resulting mixture was separated by recrystallization from $CHCl_3$ and column chromatography (eluent $CHCl_3$), which allows the isolation of compounds **2b** and **3a**. It should be noted that under similar conditions, 2,2-disubstituted aziridine **1c** reacts with the formation of exclusively *N*-[2-(adamantan-1-yl)-2-hydroxypropyl]-2,2,2-trifluoroacetamide (**3b**), which can be explained by the formation of a tertiary carbocation stabilized by the trifluoroacetate anion, and subsequent hydrolysis of the resulting intermediate (Scheme 1).

It is known that the 3-homoadamantyl and 1-adamantylcarbinyl systems form carbocations under certain conditions and easily undergo transformations of the carbon skeleton.[21–24] Thus, the presumptive mechanism for the formation of compounds **2a**,**b** includes *N*-acylation followed by the opening of the aziridine ring and the formation of adamantyl carbinyl cation **A**. Adamantyl carbinyl cation **A** rearranges into a more stable homoadamantyl cation **B**, which forms dihydro-1,3-oxazines **2a**,**b** upon further intramolecular heterocyclization (Scheme 2).

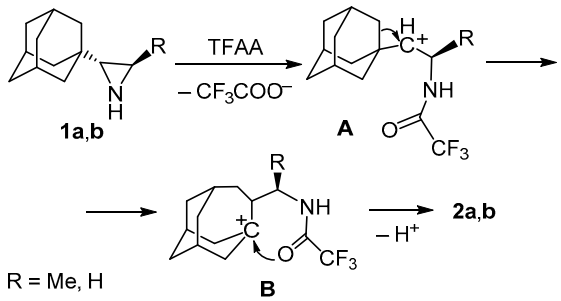
The IR spectra of compounds **2a**,**b** contain an intense absorption band at 1701–1702 cm^{-1}, characteristic of the C=N bond. The data of ^1H and ^{13}C NMR spectroscopy of compound **2a** confirm the formation of only one

Scheme 1



diastereoisomer with the (4*R**,4a*R**) configuration. Such stereospecificity in the process of skeletal rearrangement is characteristic of transformations involving nonclassical carbocations, including a number of cage compounds.[21–24] The molecular structure of compound **2a** was also determined by X-ray structural analysis, the data of which confirmed the (4*R**,4a*R**) configuration of dihydro-1,3-oxazine **2a** (Fig. 3).

Scheme 2



It should be noted that the reaction of *N*-trifluoroacetylaziridine **4** with $BF_3 \cdot Et_2O$ in CH_2Cl_2 leads to the formation of a mixture of products, compound **2a** and amide **5** in a 1:1 ratio according to GC/MS and NMR spectroscopy (Scheme 3). Carrying out the reaction at elevated temperature (40°C) for 10 h leads to amide **5** as the main product in 51% yield.

Acid hydrolysis of 2-(trifluoromethyl)dihydro-1,3-oxazine **2a** in 18% aqueous HCl (100°C) leads to the formation of amino alcohol **6** isolated in the form of hydrochloride. With longer heating times in concentrated HCl (100°C, 7 h), the formation of amino alcohol **6** and vicinal chloramine **7** is observed in a 2:1 ratio (Scheme 4). After recrystallization from EtOAc–Et_2O solvent mixture, compounds **6** and **7** were isolated and characterized. We found that this reaction is accompanied by reverse

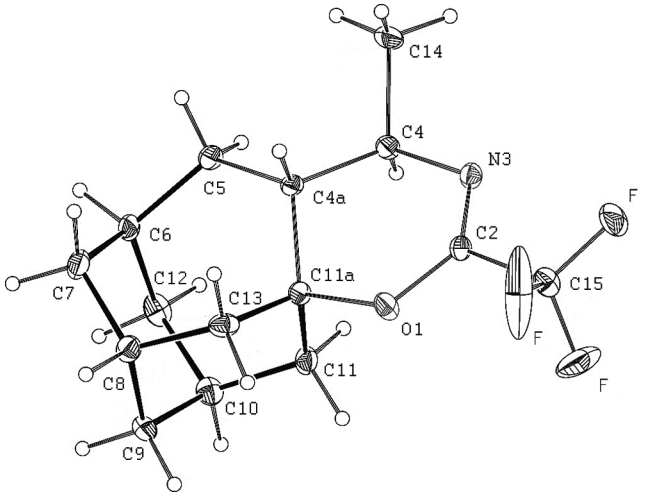
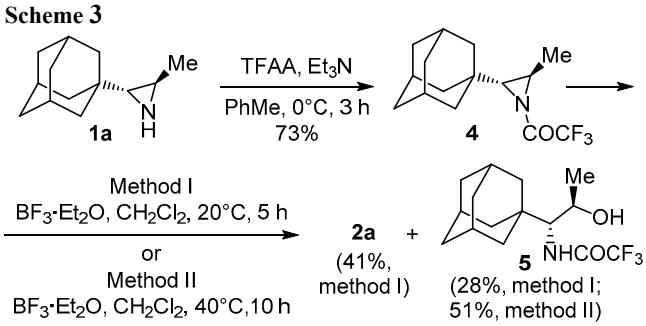


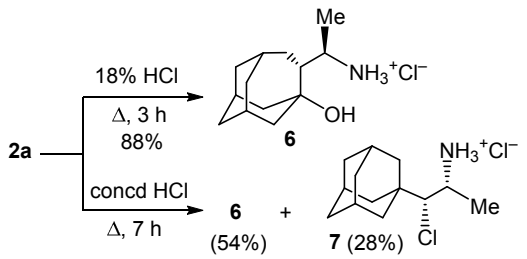
Figure 3. Molecular structure of compound **2a** with atoms represented as thermal vibration ellipsoids of 30% probability.

Scheme 3



transformation of the carbon skeleton of the homoadamantane framework, which leads to the formation of a probably more thermodynamically stable product **7** with an adamantyl substituent.[26]

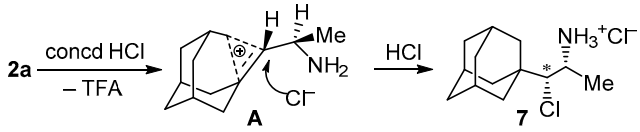
Scheme 4



We believe that the 1,3-oxazine ring opens at the C–O bond with the formation of the nonclassical carbocation **A**. Subsequent addition of the chloride anion to carbocation **A** leads to the formation of a new stereocenter and product **7** with the (1*R**,2*R**) configuration (Scheme 5).

In the IR spectrum of vicinal chloramine **7**, a band of stretching vibrations of the C–Cl bond at 740 cm^{-1} can be observed. In the mass spectrum of chloramine **7**, isolated in the form of the free base, the molecular ion exhibits an isotopic distribution characteristic of compounds with one chlorine atom (peaks with *m*/*z* 227 and 229 in a ratio of 3:1). A peak of a fragmentation ion with *m*/*z* 192, indicative of the elimination of a chlorine atom, is also observed.

Scheme 5



To conclude, the structural transformations of adamantyl-containing aziridine derivatives were studied and previously unknown 2-(trifluoromethyl)dihydro-1,3-oxazines condensed with homoadamantane were obtained. It was found that the formation of 2-(trifluoromethyl)-dihydro-1,3-oxazines depends on the structure of the starting aziridine.

Experimental

IR spectra were registered on a Shimadzu IR Affinity-1 spectrometer equipped with a Specac Quest ATR attachment. ^1H and ^{13}C NMR spectra (400 and 100 MHz, respectively), as well as DEPT-135, ^1H–^{13}C HMQC, and HMBC spectra were acquired on a JEOL JNM ECX-400 spectrometer in DMSO-d_6 (compounds **5**, **6**) and $CDCl_3$ (remaining compounds), with TMS as internal standard. Mass spectra were recorded on a Thermo Finnigan DSQ (GC/MS) system, EI ionization (70 eV), quartz column DB-5MS 30 m × 0.32 mm, 80–340°C column temperature (20°C/min heating rate), 250°C evaporator temperature, helium carrier gas. Elemental analysis was performed on a Euro Vector EA-3000 CHNS-analyzer using L-cystine as standard. Melting points were determined on an SRS OptiMelt MPA100 apparatus. Monitoring of the reaction progress was done by TLC on Merck TLC Silica gel 60 plates, visualization in iodine vapors. Merck M-60 silica gel was used for column chromatography.

Synthesis of dihydro-1,3-oxazines 2a,b and 3a,b (General method). Trifluoroacetic anhydride (5.2 mmol) was added with stirring to a mixture of aziridine **1a**,**b** (5.2 mmol) and PhMe (6 ml) at 5°C. Stirring was continued at 5°C for 1 h. H_2O (10 ml) was then added, the organic layer was separated, and the aqueous phase was extracted with PhMe (3×5 ml). The combined extracts were washed with H_2O, then aqueous $NaHCO_3$, dried over Na_2SO_4, and evaporated under reduced pressure.

(4*R,4a*R**)-4-Methyl-2-(trifluoromethyl)-4a,5,6,7,8,9,10,11-octahydro-4*H*-6,10:8,11a-dimethanocyclonona[*e*][1,3]-oxazine (2a)**. PhMe was evaporated under reduced pressure to a small volume, the formed precipitate was filtered off and washed with petroleum ether. Yield 1.17 g (78%), colorless crystals, mp 120–121°C (PhMe). IR spectrum, ν, cm^{-1}: 2904, 2854 (C–H), 1701 (C=N), 1186, 1165, 1134 (C–F). ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.21 (1H, dt, ^2J = 12.6, ^3J = 5.5, 5-CH_2); 1.25 (3H, d, ^3J = 6.9, CH_3); 1.35–1.40 (1H, m, 7-CH_2); 1.46–1.50 (1H, m, 12-CH_2); 1.51–1.56 (2H, m, 9-CH_2); 1.58–1.63 (1H, m, 4a-CH); 1.70–1.76 (1H, m, 13-CH_2); 1.78–1.80 (1H, m, 11-CH_2); 1.82–1.86 (1H, m, 12-CH_2); 1.86–1.89 (1H, m, 7-CH_2); 1.91–1.94 (1H, m, 11-CH_2); 1.99 (1H, sept, ^3J = 3.7, 8-CH); 2.04 (1H, sept, ^3J = 3.0, 10-CH); 2.10–2.14 (1H, m, 13-CH_2); 2.15–2.18 (1H, m, 6-CH); 2.18–2.22 (1H, m, 5-CH_2); 3.15 (1H, qdd, ^3J = 6.9, ^4J = 3.7, ^4J = 1.8, 4-CH). ^{13}C NMR spectrum, δ, ppm (*J*, Hz): 20.5 (CH_3); 26.9

(C-10); 27.5 (C-8); 30.9 (C-6); 35.2 (C-9); 35.5 (C-12); 37.4 (C-5); 38.9 (C-7); 39.4 (C-11); 46.6 (C-13); 46.9 (C-4a); 54.1 (C-4); 82.2 (C-11a); 116.9 (q, $^1J_{CF}$ = 276.0, CF_3); 146.8 (q, $^2J_{CF}$ = 37.0, C-2). Mass spectrum, *m/z* (I_{rel}, %): 287 $[M]^+$ (8), 148 $[HomoAd]^+$ (100), 119 (15), 105 (38), 91 (52), 79 (34), 70 (25). Found, %: C 62.68; H 6.99; N 4.90. $C_{15}H_{20}F_3NO$. Calculated, %: C 62.70; H 7.02; N 4.87.

2-(Trifluoromethyl)-4a,5,6,7,8,9,10,11-octahydro-4*H*-6,10:8,11a-dimethanocyclononа[*e*][1,3]oxazine (2b). The resulting mixture of products **2b** and **3a** was recrystallized from $CHCl_3$, the filtrate was evaporated under reduced pressure, the obtained residue was purified by column chromatography, eluent $CHCl_3$. Yield 0.67 g (45%), light-yellow crystals, mp 98–100°C. IR spectrum, ν, cm^{-1}: 2920, 2850 (C–H), 1702 (C=N), 1201, 1178, 1159 (C–F). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.09–1.14 (1H, m, 12-CH_2); 1.40–1.44 (1H, m, 7-CH_2); 1.48–1.52 (1H, m, 11-CH_2); 1.52–1.55 (2H, m, 5-CH_2); 1.56–1.70 (1H, m, 9-CH_2); 1.75–1.83 (2H, m, 7,9-CH_2); 1.93–1.97 (2H, m, 13-CH_2); 2.01–2.05 (2H, m, 6,10-CH); 2.05–2.08 (2H, m, 4a-CH, 12-CH_2); 2.08–2.14 (2H, m, 8-CH, 11-CH_2); 3.17 (1H, dd, ^2J = 13.9, ^3J = 8.0, 4-CH_2); 3.52 (1H, dd, ^2J = 13.9, ^3J = 8.7, 4-CH_2). ^{13}C NMR spectrum, δ, ppm (*J*, Hz): 27.8 (C-10); 28.0 (C-6); 30.3 (C-8); 34.8 (C-9); 36.2 (C-5); 36.8 (C-12); 39.4 (C-7); 41.3 (C-11); 43.5 (C-4); 47.0 (C-4a); 51.6 (C-13); 76.2 (C-11a); 116.1 (q, $^1J_{CF}$ = 287.0, CF_3), 156.7 (q, $^2J_{CF}$ = 36.0, C-2). Mass spectrum, *m/z* (I_{rel}, %): 273 $[M]^+$ (66), 204 $[M–CF_3]^+$ (33), 160 $[M–NC(CF_3)O]^+$ (32), 148 $[HomoAd]^+$ (68), 135 (73), 119 (27), 105 (64), 91 (100), 79 (86), 69 $[CF_3]^+$ (54), 56 (68). Found, %: C 61.51; H 6.60; N 5.18. $C_{14}H_{18}F_3NO$. Calculated, %: C 61.53; H 6.64; N 5.13.

***N*-[1-(Adamantan-1-yl)-2-hydroxyethyl]-2,2,2-trifluoroacetamide (3a)**. The resulting mixture of products **2b** and **3a** was recrystallized from $CHCl_3$. The formed precipitate was filtered off, the resulting product was washed with $CHCl_3$, and air-dried. Yield 0.62 g (39%), colorless crystals, mp 154–155 °C ($CHCl_3$). IR spectrum, ν, cm^{-1}: 3429 (N–H), 3230 (O–H), 2900, 2852 (C–H), 1701 (C=O), 1211, 1184, 1155 (C–F), 1029 (C–O). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.58–1.74 (12H, m, CH_2 Ad); 1.93 (1H, br. s, OH); 1.95–2.04 (3H, m, CH Ad); 3.69 (1H, ddd, ^3J = 7.6, ^3J = 6.2, ^3J = 3.2, CHN); 3.76 (1H, dd, ^2J = 11.5, ^3J = 6.2, CH_2O); 3.85 (1H, dd, ^2J = 11.5, ^3J = 3.2, CH_2O); 6.51 (1H, d, ^3J = 7.6, NH). ^{13}C NMR spectrum, δ, ppm (*J*, Hz): 28.2 (CH Ad); 36.0 (C Ad); 36.8 (CH_2 Ad); 39.1(CH_2 Ad); 60.1 (CHN); 60.6 (CH_2O); 116.2 (q, $^1J_{CF}$ = 291.4, CF_3); 157.9 (q, $^2J_{CF}$ = 36.4, C=O). Mass spectrum, *m/z* (I_{rel}, %): 291 $[M]^+$ (1), 260 $[M–CH_2OH]^+$ (10), 135 $[Ad]^+$ (100), 107 (7), 93 (18), 79 (20), 69 $[CF_3]^+$ (10), 55 (6). Found, %: C 57.69; H 6.90; N 4.83. $C_{14}H_{20}F_3NO_2$. Calculated, %: C 57.72; H 6.92; N 4.81.

***N*-[2-(Adamantan-1-yl)-2-hydroxypropyl]-2,2,2-trifluoroacetamide (3b)**. Yield 1.09 g (69%), mp 133–135°C (hexane) (mp 130–132°C (PhMe)[27]).

1-[(2*R,3*R**)-2-(Adamantan-1-yl)-3-methylaziridin-1-yl]-2,2,2-trifluoroethan-1-one (4)**. TFAA (0.75 ml, 5.4 mmol) was added to a mixture of aziridine **1a** (1 g, 5.2 mmol) and Et_3N (0.73 ml, 5.2 mmol) in PhMe (6 ml) at 0°C. The reaction mixture was stirred at 0°C for 3 h. It was then poured into H_2O (20 ml), extracted with PhMe (3×5 ml), the combined extracts were washed with H_2O and dried over Na_2SO_4. The solvent was evaporated under reduced pressure, and the obtained crystals were washed with petroleum ether. Yield 1.1 g (73%), mp 108–110°C (PhMe). IR spectrum, ν, cm^{-1}: 2902, 2852 (C–H), 1697 (C=O), 1203, 1153, 1134 (C–F). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.33 (3H, d, ^3J = 5.5, CH_3); 1.51–1.71 (12H, m, CH_2 Ad); 1.94–2.00 (3H, m, CH Ad); 2.18 (1H, d, ^3J = 3.4, AdCHN); 2.89 (1H, qd, ^3J = 5.5, ^3J = 3.4, $CH_3C\underline{H}N$). ^{13}C NMR spectrum, δ, ppm (*J*, Hz): 17.0 (CH_3); 28.0 (CH Ad); 32.5 (C Ad); 36.8 (CH_2 Ad); 37.4 ($\underline{C}HCH_3$); 39.2 (CH_2 Ad); 54.3 (Ad$\underline{C}$H); 115.9 (q, $^1J_{CF}$ = 288.0, CF_3); 164.9 (q, $^2J_{CF}$ = 37.0, C=O). Mass spectrum, *m/z* (I_{rel}, %): 287 $[M]^+$ (1), 152 $[M–Ad]^+$ (10), 135 $[Ad]^+$ (100), 107 (15), 93 (20), 79 (30), 69 $[CF_3]^+$ (9). Found, %: C 62.67; H 6.99; N 4.89. $C_{15}H_{20}F_3NO$. Calculated, %: C 62.70; H 7.02; N 4.87.

***N*-[(1*R**,2*R**)-1-(Adamantan-1-yl)-2-hydroxypropyl]-2,2,2-trifluoroacetamide (5)**. Method I. $BF_3·Et_2O$ (0.45 ml, 3.6 mmol) was added to a mixture of compound **4** (1 g, 3.4 mmol) and CH_2Cl_2 (15 ml). The mixture was stirred under inert atmosphere at 20°C for 5 h. The reaction mixture was poured into H_2O and extracted with CH_2Cl_2 (3×5 ml). The organic layer was washed with H_2O followed by aqueous $NaHCO_3$, dried over Na_2SO_4, and evaporated under reduced pressure. The residue was treated with a mixture of $CHCl_3$ – petroleum ether, the resulting precipitate (compound **5**) was filtered off and air-dried. The filtrate was evaporated under reduced pressure, and the residue was recrystallized from PhMe to afford compound **2a**, yield 0.41 g (41%). Yield 0.3 g (28%), white powder, mp 151–152°C. IR spectrum, ν, cm^{-1}: 3358 (N–H), 3282 (O–H), 2900, 2852 (C–H), 1697 (C=O), 1182, 1157, 1126 (C–F), 1053 (C–O). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.97 (3H, d, ^3J = 6.2, CH_3); 1.46–1.89 (12H, m, CH_2 Ad); 1.85–1.92 (3H, m, CH Ad); 3.42 (1H, dd, ^3J = 10.1, ^3J = 6.2, CHN); 3.85 (1H, sex, ^3J = 6.2, CHO); 4.56 (1H, d, ^3J = 6.2, OH); 8.70 (1H, d, ^3J = 10.1, NH). ^{13}C NMR spectrum, δ, ppm (*J*, Hz): 22.3 (CH_3); 28.4 (CH Ad); 36.5 (C Ad); 37.1 (CH_2 Ad); 39.3(CH_2 Ad); 63.9 (CHN); 65.1 (CHO); 116.4 (q, $^1J_{CF}$ = 284.0, CF_3); 157.0 (q, $^2J_{CF}$ = 36.0, C=O). Mass spectrum, *m/z* (I_{rel}, %): 305 $[M]^+$ (1), 260 $[M–CH_3CHOH]^+$ (80), 135 $[Ad]^+$ (100), 119 (8), 107 (12), 91 (36), 79 (38), 69 $[CF_3]^+$ (14), 45 $[CH_3CHOH]^+$ (84). Found, %: C 58.98; H 7.23; N 4.63. $C_{15}H_{22}F_3NO_2$. Calculated, %: C 59.00; H 7.26, N 4.59.

(1*R)-1-((4*R**)-3-Hydroxytricyclo[4.3.1.1^{3,8}]undecan-4-yl)ethan-1-ammonium chloride (6)**. A mixture of dihydro-1,3-oxazine **2a** (0.4 g, 1.4 mmol) and 18% aqueous HCl (10 ml) was heated at 100°C for 3 h. The reaction mixture was evaporated under reduced pressure, the residue was recrystallized from MeOH. Yield 0.3 g (88%), white powder, mp 200°C (decomp., MeOH). IR spectrum, ν, cm^{-1}: 3425 (O–H), 3045 (NH_3^+), 2900, 2848 (C–H), 1103 (C–O). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.13 (3H, d, ^3J = 7.9, CH_3); 1.20–2.61 (16H, m, CH_2 HomoAd, CH HomoAd); 3.82 (1H, q, ^3J = 7.9, CHN); 5.12 (1H, br. s, OH); 7.90 (3H, br. s, NH). ^{13}C NMR spectrum, δ, ppm: 16.8 (CH_3); 27.5, 28.3, 29.9 (CH HomoAd); 33.1, 33.3, 36.3, 40.9, 41.0, 49.2 (CH_2 HomoAd); 49.7 (CH HomoAd); 52.0 (CHN); 74.2 (CO). Found, %: C 63.49; H 9.81; N 5.74. $C_{13}H_{24}ClNO$. Calculated, %: C 63.53; H 9.84; N 5.70.

(1*R,2*R**)-1-(Adamantan-1-yl)-1-chloropropan-2-ammonium chloride (7)**. A mixture of dihydro-1,3-oxazine **2a** (1 g, 3.4 mmol) and concentrated HCl (20 ml) was heated at 100°C for 7 h. The reaction mixture was evaporated under reduced pressure, the residue was recrystallized from a mixture of EtOAc–Et_2O. The formed precipitate (compound **6**, yield 0.46 g (54%)) was filtered off, the filtrate was evaporated under reduced pressure to a small volume, the precipitate of chloramine **7** was filtered off and washed with Et_2O. Yield 0.26 g (28%), colorless crystals, mp 213°C (decomp., EtOAc). IR spectrum, ν, cm^{-1}: 3037 (NH_3^+), 2900, 2846 (C–H), 740 (C–Cl). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.55 (3H, d, ^3J = 6.4, CH_3); 1.63–1.74 (12H, m, CH_2 Ad); 1.99–2.05 (3H, m, CH Ad); 3.49 (1H, d, ^3J = 1.0, CHCl); 3.94 (1H, qd, ^3J = 6.4, ^3J = 1.0, CHN), 8.43 (3H, br. s, NH). ^{13}C NMR spectrum, δ, ppm: 20.4 (CH_3); 28.4 (CH Ad); 36.4 (CH_2 Ad); 38.1 (C Ad); 39.2 (CH_2 Ad); 46.7 (CHN); 76.0 (CHCl). Mass spectrum of the free base of **7**, *m*/*z* (I_{rel}, %): 227 $[M]^+$ (1), 192 $[M–Cl]^+$ (2), 135 $[Ad]^+$ (5), 91 (12), 77 (6), 44 $[CH_3CHNH_2]^+$ (100). Found, %: C 59.04; H 8.85; N 5.33. $C_{13}H_{23}Cl_2N$. Calculated, %:C 59.09; H 8.77; N 5.30.

X-ray structural analysis of compound 2a was performed on a Bruker APEX II CCD diffractometer. Crystals suitable for X-ray structural analysis were obtained by slow evaporation of a solution of compound **2a** in CH_2Cl_2. X-ray structural data for compound **2a** were deposited at the Cambridge Crystallographic Data Center (deposit CCDC 1415351).

This work was financially supported by the Russian Foundation for Basic Research (grants 17-03-01292, 19-03-00929) as part of the State Assignment (No. 0778-2020-0005).

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