Reactions of 3-amino-1-phenyl- and 3-amino-1-(thien-2-yl)-4,4,4-trifluorobut-2-en-1-ones with 1,2-diaminopropane and 1,2-diamino-3,3,3-trifluoropropane

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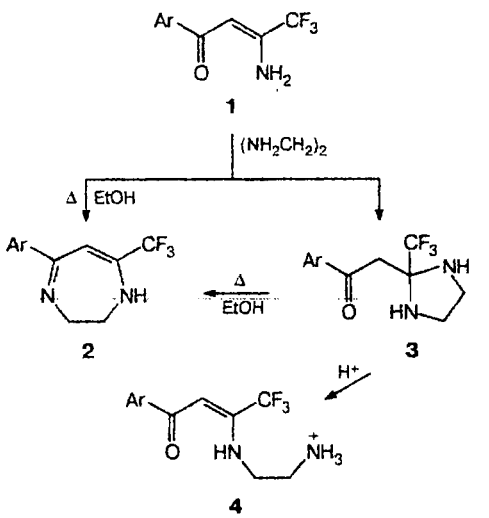
The reactions of 3-amino-1-phenyl- and 3-amino-1-(thien-2-yl)-4,4,4-trifluorobut-2-en-1-ones with 1,2-diaminopropane under kinetically controlled conditions afford mixtures of *cis* and *trans* isomers of 2-aroylmethyl-4-methyl-2-trifluoromethylimidazolidines. Analogous reactions with 1,2-diamino-3,3,3-trifluoropropane yield *cis*-2-aroylmethyl-2,4-bis(trifluoromethyl)imidazolidines.

Key words: β-amino-β-trifluoromethylvinyl ketones, 1,2-diaminopropane, 1,2-diamino-3,3,3-trifluoropropane, 2,2,4-trisubstituted imidazolidines.

It is known[1] that ethylenediamine reacts with β-amino-β-trifluoromethylvinyl ketones **1** upon boiling in alcohol or benzene simultaneously at two electrophilic centers to form 2,3-dihydro-1*H*-1,4-diazepines **2**. Aldehydes and ketones react with ethylenediamine to give 1-alkylidene(arylidene)amino-2-aminoethanes or their mixtures with 2-mono- and 2,2-disubstituted imidazolidines.[2] The reactions of perfluorinated aldehydes and hexafluoroacetone with ethylenediamine afford 2-perfluoroalkylimidazolidines[3] and 2,2-bis(trifluoromethyl)imidazolidine,[4] respectively, which exhibit various kinds of biological activity. Recently, we have demonstrated[5,6] that the reactions of 3-amino-1-aryl-4,4,4-trifluorobut-2-en-1-ones **1** with ethylenediamine under kinetically controlled conditions (at room temperature in the medium of ethylenediamine) proceeded only at the β-carbon atom to form 2-aroylmethyl-2-trifluoromethylimidazolidines **3**. The latter were converted into thermodynamically more stable dihydrodiazepines **2** upon boiling in alcohol, while in acidic medium 30—100% of **3** underwent cleavage to form aminoenones **4** containing the 2-aminoethyl group at the nitrogen atom. The formation of compounds **4** was observed by ^{1}H NMR spectroscopy, but these compounds were not isolated in individual form.[6]



This work is devoted to studies of the reactions of 3-amino-1-phenyl- (**1a**) and 3-amino-1-(thien-2-yl)-4,4,4-trifluorobut-2-en-1-ones (**1b**) with 1,2-diaminopropane and 1,2-diamino-3,3,3-trifluoropropane under kinetically controlled conditions. It was expected that reactions with the use of 1,2-diaminopropane, whose reactivity is similar to that of ethylenediamine, performed under these conditions would afford the corresponding imidazolidines, and that change of 1,2-diaminopropane for 1,2-diamino-3,3,3-trifluoropropane, in which one amino group experiences the strong electron-withdrawing effect of the trifluoromethyl substituent and, hence, possesses the lower nucleophilicity, would make it possible to terminate the reaction at the stage of transamination and to obtain intermediate aminoenones containing the 2-amino-3,3,3-trifluoropropyl substituent at the nitrogen atom. It should be noted that when undertaking this study, we lacked data on the properties of 1,2-diamino-3,3,3-trifluoropropane, which was prepared only recently.[7]

We found that the reactions of β-amino-β-trifluoromethylvinyl ketones **1a,b** with 1,2-diaminopropane proceeded at room temperature without a solvent over 20 and 5 h for **1a** and **1b**, respectively, to give, as expected,

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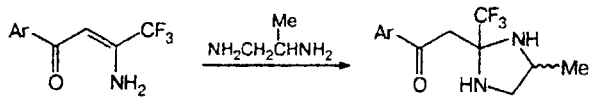
mixtures of the *cis* and *trans* isomers of imidazolidines **5a,b** with a substantial predominance of one of them. Judging from the ^{1}H NMR spectral data, the ratio of the isomers was ~9 : 1. However, the available data did not allow us to make an unambiguous conclusion about the configurations of the major and minor isomers.



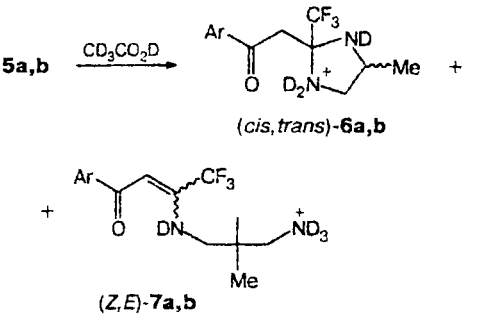
1a,b **5a,b**

Ar = Ph (**a**), 2-C_4H_3S (**b**)

The ^{1}H NMR spectra of the major isomers of imidazolidines **5a,b** have a doublet of the methyl group (at δ 1.10, J = 5.9 Hz), a one-proton triplet (at δ 2.58, J = 9.4—9.7 Hz), and a two-proton multiplet of the CH_2—CH fragment (at δ 3.17—3.36) along with signals of the aromatic protons. The exomethylene group is manifested as an AB system with the center at δ 3.31 and 3.23 (J_{AB} = 14.5 and 14.3 Hz) for **5a** and **5b**, respectively. The signals of the NH protons are so broadened that they are not observed in the spectrum of imidazolidine **5b**.

The assignment of the signals of the ring protons should be made taking into account that in such five-membered rings, the signal of the proton in the *cis* position with respect to the CH_3 group is shifted upfield by approximately δ 0.7—0.8, as in the case of 2,2-disubstituted *trans*-4,5-dimethyl-1,3-dioxolane[8] and *trans*-4,5-dimethylimidazolidine.[9] Based on this fact, the high-field triplet (at δ 2.58) should be assigned to the proton of the CH_2 group located in the *cis* position with respect to the methyl group and its triplet character indicates that the geminal and vicinal spin-spin coupling constants are equal ($J_{gem} \approx J_{vic} \approx 9.5$ Hz). Hence, J_{trans} in the imidazolidine system under consideration is ~9.5 Hz. The calculation of J_{cis} presented difficulties due to the overlap of the AB spectrum of the exomethylene CH_2 group and the multiplet of the CHH—CH fragment and gave the value of ~6.0 Hz, which agrees sufficiently well with the published data for 1,3-dioxolanes.[8]

Immediately after addition of CD_3CO_2D to a solution of compound **5a** in $CDCl_3$, 50% of *N*-deuterated imidazolidinium form **6a** was cleaved to yield aminoenone form **7a**. In this case, compound **6a** existed as a mixture of the *cis* and *trans* isomers in a ratio of ~9 : 1 and compound **7a** existed as a mixture of regioisomers with the *Z* configuration of the double bond[6] in a ratio of ~8 : 2. It should be noted that finer interactions of the protons of the endocyclic CH_2 group are manifested upon exchange of the NH protons for deuterium. In this case, the outer signals of the high-field triplet are split into quartets with J = 1.3 Hz and the central signal appears as a quintet due to the overlap of three bands of two quartets each, which is indicative of the splitting of this proton (most likely, at the fluorine atoms of the CF_3 group) into a doublet of doublets of quartets. Each signal of the doublet of doublets of the low-field proton of the endocyclic CH_2 group is also split into a quartet with J = 1.5 Hz. The presence of regioisomers of **7a** in an acidic medium can be judged from two doublets of the methyl groups (at δ 1.38 with J = 6.5 Hz and at δ 1.42 with J = 6.0 Hz) as well as from two singlets of the ethylene protons at δ 6.22 and 6.29 belonging to signals of the minor and major isomers, respectively. Taking into account the different character of the nitrogen atoms, it can be suggested that the isomer containing the 2-amino-1-methylethyl substituent at the nitrogen atom, which is formed upon cleavage of the C(2)—N(1) bond, predominates. Consequently, the salt formation, which precedes the ring opening, occurs mainly with the participation of the sterically less hindered N(1) atom.[6] An analogous situation was also observed upon addition of CD_3CO_2D to a solution of imidazolidine **5b** in $CDCl_3$ (see Experimental).



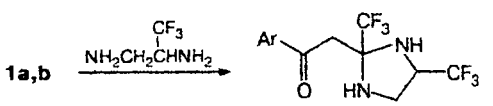
Ar = Ph (**a**), 2-C_4H_3S (**b**)

In spite of the fact that compounds **5a,b** existed as mixtures of the *cis* and *trans* isomers, the ^{19}F NMR spectra had one singlet of the CF_3 group at δ 79.32 and 79.22 for **5a** and **5b**, respectively. The signal of the CF_3 group of the minor isomer appeared as a small shoulder at the signal of the major isomer (the downfield shift is 0.17—0.08 ppm) only after addition of CD_3CO_2D. These data agree with the ^{19}F NMR spectrum of a mixture of *Z*- and *E*-phenyl 3,5-dimethyl-5-trifluoromethyl-Δ^1-pyrazoline-3-carboxylates,[10] in which the difference between the chemical shifts of the CF_3 groups is also only 0.08 ppm and the spin-spin coupling between the CF_3 and CH_3 groups is absent. Immediately after addition of CD_3CO_2D to a chloroform solution of compound **5a**, two singlets of the CF_3 groups of regioisomeric aminoenones (*Z*)-**7a** appeared at δ 95.89 and 96.03 (these singlets belong to the major and minor isomers, respectively; the ratio is 85 : 15) along with a singlet of the CF_3 group of the *N*-deuterated form of **6a** (which is present in an amount of ~40%) at δ 80.06. In addition, two low-intensity singlets (~4%) were observed at δ 93.39 and 93.12, which, apparently, belong to the CF_3 groups of the regioisomeric aminoenones (*E*)-**7a**. The ^{19}F NMR spectrum of 2-phenacyl-2-trifluoromethyl-

imidazolidine (**8**)[6] was measured for comparison. The latter had a singlet of the CF_3 group of the imidazolidine form (93%) at δ 79.63 and a singlet of the CF_3 group of the open aminoenone form (7%) at δ 90.93. After addition of CD_3CO_2D, the spectrum had three singlets at δ 80.60, 93.29, and 95.79 with an intensity ratio of 12 : 8 : 80, which were assigned to the CF_3 groups of *N*-deuterated imidazolidine and *E*- and *Z*-aminoenones containing the 2-aminoethyl substituents at the nitrogen atom, respectively. The signal at δ 93 supports the conclusion that the opening of the imidazolidine ring in the presence of acid is nonstereospecific.

The reactions of aminoenones **1a,b** with 1,2-diamino-3,3,3-trifluoropropane afforded trifluoromethylated analogs of compounds **5a,b**, *viz.*, 2-aroylmethyl-2,4-bis(trifluoromethyl)imidazolidines **9a,b**. It appeared that the replacement of the methyl group in 1,2-diaminopropane by the trifluoromethyl group results only in a decrease in the reaction rate and has no effect on the structure of the final product. This fact indicates that the introduction of the CF_3 group into the ethylenediamine molecule leads to a decrease in the nucleophilicity of the molecule as a whole, which prevented us from performing transamination selectively at the amino group remote from the trifluoromethyl substituent. The ^{19}F NMR spectra demonstrated that the reaction of aminoenone **1b** with 1,2-diamino-3,3,3-trifluoropropane was virtually completed in one week, while in the reaction with **1a**, only 25% of the reagent was consumed. We succeeded in preparing imidazolidine **9a** containing 10% of an admixture of the initial aminoenone **1a** when the reaction was performed over 3 weeks. In this connection, it is worthy of note that aminoenone **1b** containing the thien-2-yl substituent at the carbonyl group exhibits higher reactivity toward substituted ethylenediamines.

Reactions with the participation of 1,2-diamino-3,3,3-trifluoropropane, unlike those with 1,2-diaminopropane, proceed more stereoselectively, which can be judged from the one set of signals in the ^1H and ^{19}F NMR spectra of imidazolidines **9a,b**. The products are stable in an acidic medium and are not opened to form the corresponding aminoenones upon addition of CD_3CO_2D, unlike imidazolidines, which are prepared starting from ethylenediamine[6] and 1,2-diaminopropane. The higher stability of compounds **9a,b** in an acidic medium compared to compounds **5a,b** is, apparently, associated with a decrease in the basicity of the nitrogen atoms due to the presence of the second trifluoromethyl substituent, which hinders protonation of the imidazolidine ring. On the whole, according to our data, the stability of the ring in an acidic medium increases in the series of compounds **8**, **5a**, and **9a** containing the H, CH_3, and CF_3 groups, respectively, at position 4 of the ring.



cis-**9a,b**

In the ^1H NMR spectra of imidazolidines **9a,b**, the signals of the protons at the N(1) and N(3) atoms appear as a broadened singlet at δ 2.8 and a doublet at δ 3.11—3.15 (J = 8.0—7.8 Hz), respectively. Since the N(3)—H group is located between two trifluoromethyl substituents, it can be suggested that the hydrogen atom at the N(3) atom is involved in rather strong intramolecular hydrogen bonds with the fluorine atoms, which slow down the proton exchange and allow one to observe the spin-spin coupling in the CH—NH fragment. The ^1H NMR spectra of these compounds are also characterized by a septet of the methine proton (at δ 3.99—3.95, J = 7.3 Hz), which is shifted downfield compared to the signals of both methylene groups observed at δ 3.21—3.42. The splitting of the signal of the proton of the CH group into a septet indicates that the constants of spin-spin coupling of this proton with the fluorine atoms as well as with the hydrogen atoms of the CH_2 and NH groups have close values. When CD_3CO_2D was added, the signals of the protons of the NH groups disappeared and the septet was converted into a sextet with the same spin-spin coupling constant.

The ^{19}F NMR spectra of compounds **9a,b** have a pronounced doublet of quartets of the C(4)CF_3 group at δ 86.1 with J_{CH,CF_3} = 6.7 Hz and J_{CF_3,CF_3} = 2.7—2.8 Hz and a broadened quartet of the C(2)CF_3 group at δ 79.3. The mutual splitting of the signals of the trifluoromethyl substituents, which is, most likely, associated with spin-spin coupling through space,[11] indicates that these substituents are in a mutually *cis* arrangement. Previously,[12] an analogous splitting of the signals of the CF_3 groups was observed for *cis*-1,2-bis(trifluoromethyl)cyclobutanes, which is evidence in favor of the *cis* configuration of imidazolidines **9a,b**.

The IR spectra of imidazolidines **5a,b** and **9a,b** have ν(NH) absorption bands in the region of 3375—3320 cm^{-1} and ν(C=O) absorption bands in the region of 1690—1685 cm^{-1} (for compounds **5a** and **9a**) and in the region of 1670—1655 cm^{-1} (for **5b** and **9b**), which agree with their structures.

Therefore, the reactions of aminoenones **1a,b** with 1,2-diaminopropane and 1,2-diamino-3,3,3-trifluoropropane under kinetically controlled conditions proceed at different rates but afford analogous products, *viz.*, imidazolidines **5a,b** and **9a,b**. The reactions with 1,2-diamino-3,3,3-trifluoropropane are more stereoselective. Products **9a,b**, unlike **5a,b**, are stable in an acidic medium.

Experimental

The IR spectra were obtained on an IKS-29 instrument as Nujol mulls. The ^1H NMR spectra were recorded on a Bruker WM-250 spectrometer in $CDCl_3$ operating at 250.13 MHz with Me_4Si as the internal standard. The ^{19}F NMR spectra were measured in $CDCl_3$ on a Tesla BS-587A instrument operating at 75.3 MHz with C_6F_6 as the internal standard.

1,2-Diamino-3,3,3-trifluoropropane was synthesized* from 2-amino-3,3,3-trifluoro-1-nitropropene.[13] Imidazolidines **5a,b** were prepared according to a procedure reported previously.[6]

1,2-Diamino-3,3,3-trifluoropropane. A solution of 2-amino-3,3,3-trifluoro-1-nitropropene (3.72 g, 24 mmol) in anhydrous Et_2O (50 mL) was added dropwise over 1.5 h with stirring and cooling to 10 °C to a suspension of $LiAlH_4$ (3.62 g, 95 mmol) in anhydrous Et_2O (50 mL). Then the reaction mixture was stirred at ~20 °C for 48 h and treated with a 30% aqueous solution of KOH (20 mL). The organic layer was separated, the ether was distilled off, and the residue was distilled. The yield was 0.78 g (25%), b.p. 129—131 °C. ^{1}H NMR (80 MHz), δ: 1.67 (s, 4 H, 2 NH_2); 2.59—3.36 (m, 3 H, CH_2—CH). ^{19}F NMR, δ: 84.73 (d, CF_3, J = 7.3 Hz). Since 1,2-diamino-3,3,3-trifluoropropane is hygroscopic, it was additionally characterized as ditosylate.

1,2-Diamino-3,3,3-trifluoropropane ditosylate. M.p. 143 °C. Found (%): C, 46.98; H, 4.21; N, 6.44. $C_{17}H_{19}F_3N_2S_2O_4$. Calculated (%): C, 46.79; H, 4.35; N, 6.42. ^{1}H NMR (80 MHz), δ: 2.43 (s, 6 H, 2 CH_3); 3.16—3.22 (m, 2 H, CH_2); 3.99—4.13 (m, 1 H, CH); 5.53 (t, 1 H, NH—CH_2, J = 7.0 Hz); 5.99 (d, 1 H, NH—CH, J = 9.0 Hz); 7.54 (AB system, Δδ = 0.44, 8 H, 2 C_6H_4, J_{AB} = 8.0 Hz).

Preparation of imidazolidines 5a,b and 9a,b (general procedure). Aminoenones **1a,b** (1.4 mmol) were dissolved in 1,2-diaminopropane or 1,2-diamino-3,3,3-trifluoropropane (2.8 mmol) and the mixture was kept at ~20 °C. The reaction times were 20 and 5 h for imidazolidines **5a** and **5b**, respectively, and 3 and 1 weeks for **9a** and **9b**, respectively. The crystals that precipitated were washed with water, dried, and recrystallized from hexane.

4-Methyl-2-phenacyl-2-trifluoromethylimidazolidine (5a). The yield was 83%, m.p. 103—104 °C. Found (%): C, 57.17; H, 5.39; N, 10.10. $C_{13}H_{15}F_3N_2O$. Calculated (%): C, 57.35; H, 5.55; N, 10.29. IR, ν/cm^{-1}: 3375, 3330 (NH); 1690 (C=O); 1600, 1580 (benzene ring). ^{1}H NMR, δ: *major isomer* (90%): 1.10 (d, 3 H, Me, J = 5.9 Hz); 2.40—2.60 (br.s, 1 H, NH); 2.58 (t, 1 H, CHH—CH, J = 9.4 Hz); 3.00 (br.s, 1 H, NH); 3.31 (AB system, Δδ = 0.31, 2 H, CH_2, J_{AB} = 14.5 Hz); 3.17—3.35 (m, 2 H, CHH—CH); 7.45—7.53 (m, 2 H, H(3′), H(5′)); 7.57—7.64 (m, 1 H, H(4′)); 7.93—7.99 (m, 2 H, H(2′), H(6′)); *minor isomer* (10%): 1.13 (d, 3 H, Me, J = 6.4 Hz); 2.47 (t, 1 H, CHH—CH, J = 9.2 Hz). Immediately after addition of CD_3CO_2D, the *cis* and *trans* isomers of **6a** and the regioisomers of **7a** were observed in a ratio of 1 : 1; the *major isomer* of **6a** (90%): 1.12 (d, 3 H, Me, J = 6.0 Hz); 2.61 (ddq, 1 H, CHH—CH, J_{gem} = J_{vic} = 9.3 Hz, $J_{H,F}$ = 1.3 Hz); 3.37 (AB system, Δδ = 0.32, 2 H, CH_2, J_{AB} = 15.0 Hz); 3.12—3.78 (m, 2 H, CHH—CH); 7.45—7.65 (m, 3 H, H(3′), H(4′), H(5′)); 7.93—7.99 (m, 2 H, H(2′), H(6′)); the *minor isomer* of **6a** (10%): 1.18 (d, 3 H, Me, J = 6.2 Hz); the *major isomer* of **7a** (82%): 1.42 (d, 3 H, Me, J = 6.0 Hz); 3.12—3.78 (m, 3 H, CH_2—CH); 6.29 (s, 1 H, =CH); 7.41—7.65 (m, 3 H, H(3′), H(4′), H(5′)); 7.84—7.91 (m, 2 H, H(2′), H(6′)); the *minor isomer* of **7a** (18%): 1.38 (d, 3 H, Me, J = 6.5 Hz); 6.22 (s 1 H, =CH). ^{19}F NMR, δ: 79.32 (s, CF_3). Immediately after addition of CD_3CO_2D, the *cis* and *trans* isomers of **6a** and the regioisomers of **7a** were obtained in a ratio of 0.4 : 0.6; the *major isomer* of **6a** (90%): 80.06 (s, CF_3), the *minor isomer* of **6a** (10%): 80.23 (s, CF_3); the *major isomer* of **7a** (85%): 95.89 (s, CF_3), the *minor isomer* of **7a** (15%): 96.03 (s CF_3). Low-intensity singlets at δ 93.12 and 93.39 belong, apparently, to the CF_3 groups of regioisomeric aminoenones **7a** with the *E* configuration of the double bond.

4-Methyl-2-(2-thenoylmethyl)-2-trifluoromethylimidazolidine (5b). The yield was 64%, m.p. 112—113 °C. Found (%): C, 47.60; H, 4.69; N, 10.09. $C_{11}H_{13}F_3N_2OS$. Calculated (%): C, 47.47; H, 4.71; N, 10.07. IR, ν/cm^{-1}: 3345 sh, 3320 (NH); 3105, 3090 (=CH); 1665 (C=O); 1520 (thiophene ring). ^{1}H NMR, δ: the *major isomer* (87%): 1.10 (d, 3 H, Me, J = 5.9 Hz); 2.58 (t, 1 H, CHH—CH, J = 9.7 Hz); 3.23 (AB system, Δδ = 0.24, 2 H, CH_2, J_{AB} = 14.3 Hz); 3.17—3.36 (m, 2 H, CHH—CH); 7.17 (dd, 1 H, H(4′), $J_{H(4'),H(3')}$ = 3.7 Hz, $J_{H(4'),H(5')}$ = 5.1 Hz); 7.72 (dd, 1 H, H(5′), $J_{H(5'),H(3')}$ = 1.0 Hz); 7.76 (dd, 1 H, H(3′)); NH protons are not observed; the *minor isomer* (13%): 1.13 (d, 3 H, Me, J = 6.3 Hz); 2.49 (t, 1 H, CHH—CH, J = 8.7 Hz). Immediately after addition of CD_3CO_2D, the *cis* and *trans* isomers of **6b** and the regioisomers of **7b** were observed in a ratio of 2 : 1; the *major isomer* of **6b** (88%): 1.12 (d, 3 H, Me, J = 6.0 Hz); 2.60 (ddq, 1 H, CHH—CH, J_{gem} = J_{vic} = 9.5 Hz, $J_{H,F}$ = 1.2 Hz); 3.29 (AB system, Δδ = 0.24, 2 H, CH_2, J_{AB} = 15.0 Hz); 3.18—3.76 (m, 2 H, CHH—CH); 7.17 (dd, 1 H, H(4′), $J_{H(4'),H(3')}$ = 4.1 Hz, $J_{H(4'),H(5')}$ = 4.9 Hz); 7.73 (dd, 1 H, H(5′), $J_{H(5'),H(3')}$ = 1.0 Hz); 7.78 (dd, 1 H, H(3′)); the *minor isomer* of **6b** (12%): 1.17 (d, 3 H, Me, J = 6.2 Hz); the *major isomer* of **7b** (75%): 1.41 (d, 3 H, Me, J = 5.9 Hz); 3.18—3.76 (m, 3 H, CH_2—CH); 6.13 (s, 1 H, =CH); 7.12 (dd, 1 H, H(4′), $J_{H(4'),H(3')}$ = 3.6 Hz, $J_{H(4'),H(5')}$ = 5.1 Hz); 7.60 (dd, 1 H, H(5′), $J_{H(5'),H(3')}$ = 1.0 Hz); 7.66 (dd, 1 H, H(3′)); the *minor isomer* of **7b** (25%): 1.36 (d, 3 H, Me, J = 6.6 Hz); 6.12 (s, 1 H, =CH). ^{19}F NMR, δ: 79.22 (s, CF_3). Immediately after addition of CD_3CO_2D, the *cis* and *trans* isomers of **6b** and regioisomers of **7b** were obtained in a ratio of 42 : 58; the *major isomer* of **6b** (88%): 79.74 (s, CF_3), the *minor isomer* of **6b** (12%): 79.82 (s, CF_3); the *major isomer* of **7b** (82%): 95.78 (s, CF_3), the *minor isomer* of **7b** (18%): 95.90 (s, CF_3).

2-Phenacyl-2,4-bis(trifluoromethyl)imidazolidine (9a). According to the ^{1}H and ^{19}F NMR spectral data, compound **9a** contained an admixture (10%) of the initial aminoenone **1a**. The yield was 55%, m.p. 110—111 °C. Found (%): C, 48.40; H, 3.80; N, 8.44. $C_{13}H_{12}F_6N_2O$. Calculated (%): C, 47.86; H, 3.71; N, 8.59. IR, ν/cm^{-1}: 3370 (NH); 1685 (C=O); 1600, 1585 (benzene ring). ^{1}H NMR, δ: 2.83 (br.s, 1 H, N(1)H); 3.11 (d, 1 H, N(3)H, J = 8.0 Hz); 3.21—3.42 (m, 2 H, CH_2—CH); 3.41 (s, 2 H, CH_2); 3.99 (sept, 1 H, CH, J = 7.3 Hz); 7.48—7.54 (m, 2 H, H(3′), H(5′)); 7.61—7.68 (m, 1 H, H(4′)); 7.93—7.96 (m, 2 H, H(2′), H(6′)). Immediately after addition of CD_3CO_2D: 3.21—3.46 (m, 2 H, CH_2—CH); 3.45 (AB system, Δδ = 0.07, 2 H, CH_2, J_{AB} = 16.4 Hz); 4.03 (sext, 1 H, CH, J = 7.3 Hz); 7.51 (t, 2 H, H(3′), H(5′), ^oJ = 7.6 Hz); 7.64 (t, 1 H, H(4′)); 7.95 (d, 2 H, H(2′), H(6′)). ^{19}F NMR, δ: 79.39 (q, C(2)CF_3); 86.14 (dq, C(4)CF_3, J_{CH,CF_3} = 6.7 Hz, J_{CF_3,CF_3} = 2.8 Hz). The singlet of the CF_3 group of the initial aminoenone **1a** is observed at δ 90.21.

2-(2-Thenoylmethyl)-2,4-bis(trifluoromethyl)imidazolidine (9b). The yield was 35%, m.p. 109—110 °C. Found (%): C, 39.57; H, 3.22; N, 8.38. $C_{11}H_{10}F_6N_2OS$. Calculated (%): C, 39.76; H, 3.03; N, 8.43. IR, ν/cm^{-1}: 3360 (NH); 3120 (=CH); 1670, 1655 (C=O); 1520 (thiophene ring). ^{1}H NMR, δ: 2.82 (br.s, 1 H, N(1)H); 3.15 (d, 1 H, N(3)H, J = 7.8 Hz); 3.20—3.39 (m, 2 H, CH_2—CH); 3.31 (AB system, Δδ = 0.06, 2 H, CH_2, J_{AB} = 15.6 Hz); 3.95 (sept, 1 H, CH, J = 7.3 Hz); 7.19 (dd, 1 H, H(4′), $J_{H(4'),H(3')}$ = 4.0 Hz, $J_{H(4'),H(5')}$ = 4.9 Hz); 7.75 (dd, 1 H, H(3′), $J_{H(3'),H(5')}$ = 1.3 Hz); 7.76 (dd, 1 H, H(5′)). Immediately after addition of CD_3CO_2D: 3.18—3.36 (m, 2 H, CH_2—CH); 3.32 (AB system, Δδ = 0.07, 2 H, CH_2, J_{AB} = 15.5 Hz); 3.95 (sext, 1 H, CH, J = 7.3 Hz);

* This experiment was carried out with the participation of M. V. Nikonov.

7.18 (dd, 1 H, H(4'), $J_{H(4'),H(3')}$ = 3.9 Hz, $J_{H(4'),H(5')}$ = 4.9 Hz); 7.75 (dd, 1 H, H(5'), $J_{H(5'),H(3')}$ = 1.0 Hz); 7.76 (dd, 1 H, H(3')). ^{19}F NMR, δ: 79.34 (q, C(2)CF_3); 86.03 (dq, C(4)CF_3, J_{CH,CF_3} = 6.7 Hz, J_{CF_3,CF_3} = 2.7 Hz).

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