Reactions of aliphatic β-amino-β-(trichloromethyl)vinyl ketones with ethylenediamine. Synthesis and structures of 2-acetonylideneimidazolidines

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Reactions of aliphatic β-amino-β-(trichloromethyl)vinyl ketones with an excess of ethylenediamine at room temperature afford substituted 2-acetonylideneimidazolidines. The structure of 2-pivaloylmethyleneimidazolidine was established by X-ray diffraction analysis.

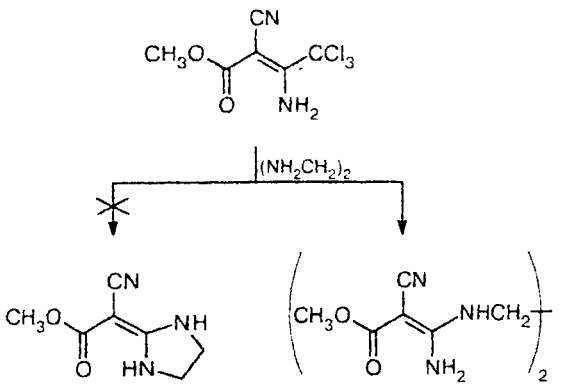
Key words: aliphatic β-amino-β-(trichloromethyl)vinyl ketones, ethylenediamine, substituted 2-acetonylideneimidazolidines; X-ray diffraction analysis.

Recently,[1,2] we have demonstrated that the reactions of aliphatic β-amino-β-(trifluoromethyl)vinyl ketones with ethylenediamine (EDA) at room temperature without a solvent afford thermodynamically more stable 2,3-dihydro-1*H*-1,4-diazepines, whereas these reactions with compounds containing sterically hindered carbonyl groups yield 2,2-disubstituted imidazolidines, which are kinetically controlled products. In this connection, it was of interest to compare the behavior of CF_3- and CCl_3-containing β-aminovinyl ketones in reactions with EDA under kinetically controlled conditions.

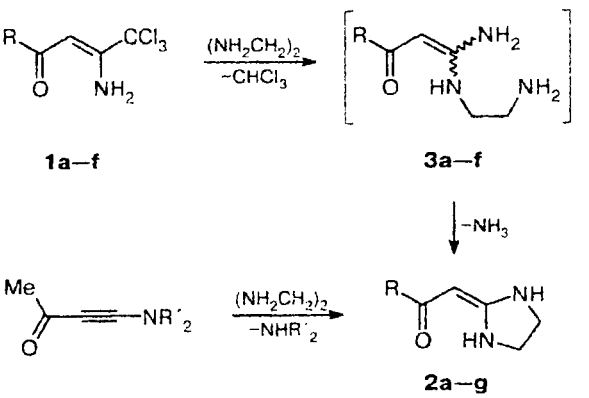
It is known that products of condensation of trichloroacetonitrile with benzoylacetonitrile,[3,4] cyanoacetic ester, or maleic ester[3,5] react with primary amines and hydrazine hydrate with the replacement of the CCl_3 group to form 1,1-diaminoethylenes[3,5] and pyrazoles,[3–6] respectively. The reaction of methyl 3-amino-4,4,4-trichloro-2-cyano-2-butenoate with EDA also proceeded with the replacement of the CCl_3 group and was accompanied by an intermolecular reaction to form a bis-adduct[3] (Scheme 1). In this case, intramolecular cyclization of intermediate ketene aminal giving rise to a 2-methyleneimidazolidine derivative was not observed.

In this work, we studied the reactions of β-amino-β-(trichloromethyl)vinyl ketones[7–9] **1a–f** with EDA and found that these reactions also proceeded as double nucleophilic attack at the β-carbon atom (Scheme 2).

Scheme 1



Scheme 2



R = Bu^t (**a**); cyclohexyl (**b**); Me_2C—OH (**c**); Et(Me)C—OH (**d**); Bu^t(Me)C—OH (**e**); $Me_2C(OH)CH_2$ (**f**); Me (**g**)

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However, these reactions, unlike reactions of CF_3-containing aminoenones, were accompanied by replacement not only of the amino group but also of the trichloromethyl fragment, giving rise to substituted 2-acetonylideneimidazolidines **2a—f** (see the preliminary communication[10]).

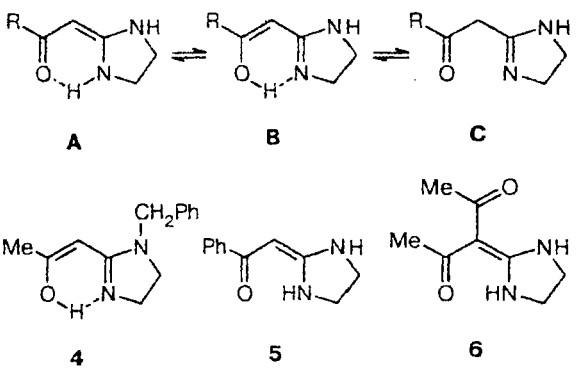
Previously, 2-acetonylideneimidazolidine (**2g**) has been prepared by the reaction of EDA with 4-dialkylamino-3-butyn-2-ones.[11] 2-Phenacylideneimidazolidine was synthesized by extrusion of sulfur from 2-phenacylthio-Δ^2-imidazoline under the action of triphenylphosphine as a thiophilic reagent[12,13] as well as by the reaction of EDA with dithioacetal of the corresponding α-oxoketene.[14] Recently, we have demonstrated that 2-(2-hydroxyaroylmethylene)imidazolidines, which have been obtained for the first time as by-products in reactions of EDA with chromone-3-carbonitriles,[15] were formed in high yields from 2-trichloromethylchromones[16] and in low yields from 3-amino-4,4,4-trichloro-1-(2-hydroxyaryl)-2-buten-1-ones.[16]

Taking into account the results of the study,[3] it can be suggested that the reactions of aminoenones **1a—f** with EDA begin with the replacement of the CCl_3 group through intermediate ketene aminals **3a—f**, which subsequently give compounds **2a—f** as a result of intramolecular replacement of the NH_2 group. The long reaction times (6—8 days) and low yields of the products (15—50%) are attributable to the fact that cyclization of intermediate aminals **3a—f** is hindered because NH_2 is a reluctant leaving group. In the reaction of EDA with aminoenone **1a**, we isolated not only individual imidazolidine **2a**, but also its mixture with a compound to which the structure of aminal **3a** was assigned based on the data of ^{1}H NMR spectroscopy. This provides support for the above-considered scheme of the reaction. It should also be noted that it was not the purpose of this work to optimize the reaction conditions, and the reaction was performed at room temperature without a solvent, *i.e.*, under conditions analogous to those used in the reactions of β-amino-β-(trifluoromethyl)vinyl ketones with EDA.[2]

2-Acylmethyleneimidazolidines possess a high electron density at the *exo*-methylene carbon atom. In many recent studies, this property has been used in the synthesis of various heterocyclic compounds, which are difficultly accessible by other methods (see Ref. 17 and references therein). However, it should be noted that the available data on the structures of 2-acylmethyleneimidazolidines are very contradictory.

Theoretically, imidazolidines **2**, like β-aminovinyl ketones, can exist in three tautomeric forms, *viz.*, in keto-enamine (**A**), imino-enol (**B**), and keto-imine (**C**) forms. However, the content of the latter (judging from the absence of the signal for the *exo*-methylene group in the ^{1}H NMR spectra of the specimens under study) was no higher than 5%.

Scheme 3



Previously,[11] compound **2g** has been described as an enol tautomer of type **B** by analogy with 1-benzyl-2-(2-hydroxyprop-1-enyl)-4,5-dihydroimidazole (**4**). This structure was assigned to compound **2g** based on the spectral and crystallographic data.[18] However, it should be noted that the data reported[11,18] for compounds **2g** and **4** do not contradict their keto-enamine structure (**A**) because bands at 3300 and 3270 cm^{-1} and chemical shifts at δ 9.1 and 9.5, which were assigned to the OH group, may be equally well attributed to the NH group involved in intramolecular hydrogen bonding. The crystallographic data[18] are indicative of electron delocalization over bonds in the crystals of dihydroimidazole **4**, but they do not provide support for the conclusion that compound **4** has the imino-enol structure (**B**) because the position of the hydrogen atom (N—H or O—H) was not established. Moreover, the signals of the CH_3 groups in the ^{1}H NMR spectra of compounds **2g** and **4** were described as singlets, which signifies the absence of allylic splitting between the ethylene hydrogen atom and the methyl group generally observed in the enol form of type **B** for such compounds as 2-pyridylacetone.[19]

Unlike 2-acetonylideneimidazolidines **2g**[11] and **4**,[18] described as imino-enol tautomers (**B**) both in the crystalline state and in $CDCl_3$ solutions, 2-phenacylideneimidazolidine (**5**) and its benzene-substituted analogs were described only as keto-enamine tautomers (**A**) in all studies[12—14,17] without discussion. The results of X-ray diffraction analysis of the crystals of 2-phenacylideneimidazolidine (**5**)[20] count in favor of structure **A** (see below).

We performed X-ray diffraction study of 2-(pivaloylmethylene)imidazolidine (**2a**) (Fig. 1).

The five-membered heterocycle adopts a half-chair conformation with the C(2) and C(3) atoms deviating from the N(2)C(1)N(1) plane by −0.19(2) Å and +0.13(2) Å, respectively. The fragment of the molecule consisting of the N(1), C(1), N(2), C(4), C(5), O(1), and C(6) atoms is virtually planar; the average deviation of the atoms from the plane is 0.025(6) Å.

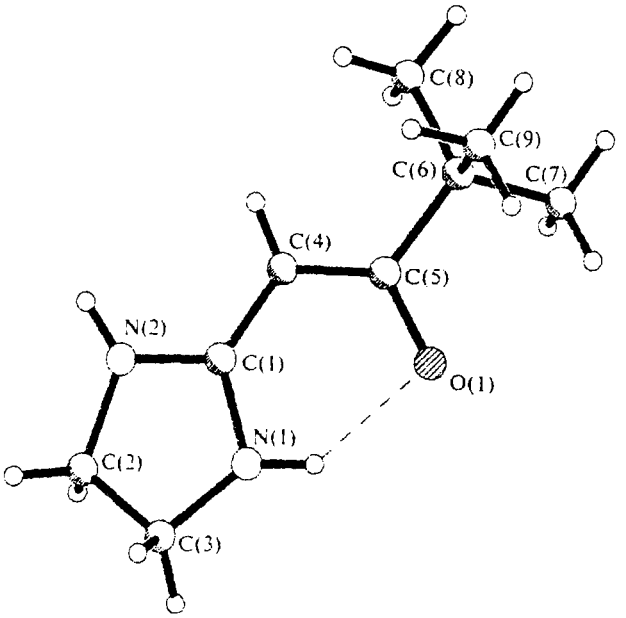


Fig. 1. Overall view of the molecule of imidazolidine **2a**.

In the molecule of compound **2a**, the H(N(1)) atom, which was located from the electron density synthesis, is involved in the intramolecular N(1)—H(N(1))...O(1) hydrogen bond with the O(1) atom (N(1)—H(N(1)), 0.93(5) Å; N(1)...O(1), 2.704(7) Å; H(N(1))...O(1), 1.93(5) Å; the N(1)—H(N(1))...O(1) angle is 139(4)°). It was demonstrated[21] that the formation of an intramolecular hydrogen bond favors the electron density delocalization and redistribution of the bond lengths within the H(N(1))—N(1)—C(1)=C(4)—C(5)=O(1) system as well as the flattening of the latter. Actually, this fragment in molecule **2a** is planar (the average deviation from the mean plane is 0.026(6) Å), the lengths of the C(1)=C(4) double bond (1.362(7) Å) and, particularly, of the C(5)=O(1) double bond (1.306(6) Å) are noticeably longer than the standard values (1.331(9) and 1.210(8) Å for the C=C and C=O bonds, respectively), whereas the single bonds N(1)—C(1) (1.365(6) Å) and C(4)—C(5) (1.387(6) Å) are substantially shorter than the standard values (1.465(18) and 1.475(16) Å for the C—C and C—N bonds, respectively).[22]

To compare our results with the structures studied previously, we searched for structures which contain a fragment analogous to that under consideration in tautomer **A** of ylideneimidazolidine **2a**, in the Cambridge Structural Database (CSD, April 1999). The intramolecular N—H...O hydrogen bond and the N(2) and C(3) atoms were also specified in the course of the search. Fourteen examples of the occurrence of the fragment of interest were found in 10 structures. The differences in the distances in question vary in the following ranges (using our notations): 2.525—2.871 Å (the average value is 2.644 Å) for N(1)...O(1), 1.593—2.295 Å (1.880 Å) for H(N(1))...O(1), 1.220—1.295 Å (1.249 Å) for C(5)=O(1), 1.384—1.493 Å (1.433 Å) for C(4)—C(5), 1.376—1.455 Å (1.411 Å) for C(1)=C(4), and 1.324—1.386 Å (1.365 Å) for N(1)—C(1). As can be seen from the above values, the corresponding bond lengths and distances in compound **2a** fall within (to within the experimental error) the above-mentioned ranges, *i.e.*, the structure of molecule **2a** can be considered as tautomer **A**. However, it should be noted that the C(5)=O(1) bond is noticeably elongated, whereas the C(1)=C(4) bond has the shortest length of all the known values.

Among the crystal structures under examination, two structures contain molecules with the conjugated fragment, which is exactly identical to that in imidazolidine **2a**, *viz.*, 2-phenacylideneimidazolidine (**5**)[20] and 3-(2-imidazolidinylidene)-2,4-pentanedione (**6**).[23] Molecule **6** contains two virtually identical ketoenamine fragments with the intramolecular N—H...O hydrogen bond, whereas molecule **5** contains only one such fragment. The parameters of the intramolecular hydrogen bonds are close to those observed in compound **2a** (N—H are 0.99 and 0.83 Å, N...O are 2.730 and 2.593 Å, H...O are 2.10 and 1.99 Å, and the N—H...O angles are 119° and 128° in compounds **5** and **6**, respectively). The bond lengths and bond angles for these fragments in the structures of **5** and **6** are given in Table 1. In all three cases (compounds **2a**, **5**, and **6**), the formally double C=C bonds are elongated, which was attributed[23] to the cooperative effect of the electron-donating character of the imidazolidine ring and the electron-withdrawing properties of the acetyl groups, whereas the observed strengthening of the single N—C and C—C bonds and weakening of the double C=O bond were attributed to π-conjugation. In all three compounds, the oxygen atom is involved both in intramolecular and intermolecular O...H—N hydrogen bonds, which also favors the weakening of the C=O bond. Analysis of the data for compounds **2a**, **5**, and **6** demonstrated that the geometry of imidazolidine **2a**, apparently, corresponds to the ketoenamine tautomer (**A**) with strong electron density delocalization in the N_2C=C—C=O fragment.

In the crystal, molecules **2a** related by the 2_1 axis are linked in chains through weak intermolecular N(2)—H(2N)...O(1) hydrogen bonds (N(2)—H(2N), 0.86 Å; N(2)...O(1), 2.815(6) Å; H(2N)...O(1), 2.04 Å; the N(2)—H(2N)...O(1) angle is 150°) (Fig. 2). The chains are arranged in layers parallel to the crystallographic plane *bc*. The adjacent chains are linked *via* van der Waals interactions.

The ^{1}H NMR spectrum of compound **2a** has two multiplets for the protons of the CH_2 groups of the AA'BB' spin system of the imidazolidine ring with centers at δ 3.51 and 3.67, a singlet for the vinyl proton at δ 4.89, and broadened signals for the protons of the NH groups at δ 4.83 and 9.34, the latter belonging to the atom involved in intramolecular hydrogen bonding.

Table 1. Bond lengths (*d*) and bond angles (ω) for compounds **2a**, **5**, and **6**

Parameter	2a	5	6
Bond		*d*/Å	
O(1)—C(5)	1.306(6)	1.241	1.243(3)
N(1)—C(1)	1.365(6)	1.338	1.324(3)
N(2)—C(1)	1.353(6)	1.328	1.329(3)
C(1)—C(4)	1.362(7)	1.403	1.451(3)
C(4)—C(5)	1.387(6)	1.384	1.448(3)
N(1)—C(3)	1.429(6)		
N(2)—C(2)	1.445(6)		
C(2)—C(3)	1.529(7)		
C(5)—C(6)	1.525(7)		
C(6)—C(8)	1.522(7)		
C(6)—C(9)	1.526(7)		
C(6)—C(7)	1.525(7)		
Angle		ω/deg	
N(2)—C(1)—N(1)	107.3(6)	109.2	108.6(2)
N(1)—C(1)—C(4)	127.3(7)	124.9	125.7(2)
C(1)—C(4)—C(5)	122.9(6)	121.9	117.2(2)
O(1)—C(5)—C(4)	122.1(6)	125.2	121.4(2)
C(1)—N(1)—C(3)	112.8(6)		
C(1)—N(2)—C(2)	111.4(5)		
N(2)—C(1)—C(4)	125.4(6)		
N(2)—C(2)—C(3)	102.9(5)		
N(1)—C(3)—C(2)	101.6(5)		
O(1)—C(5)—C(6)	115.2(6)		
C(4)—C(5)—C(6)	122.5(6)		
C(5)—C(6)—C(8)	112.4(6)		
C(5)—C(6)—C(9)	105.8(5)		
C(8)—C(6)—C(9)	109.8(5)		
C(5)—C(6)—C(7)	109.1(5)		
C(8)—C(6)—C(7)	109.6(5)		
C(9)—C(6)—C(7)	110.0(5)		

Note. For compound **6**, the average values for two keto-enamine fragments are given.

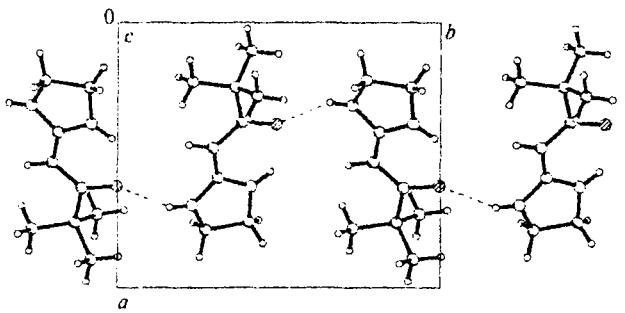
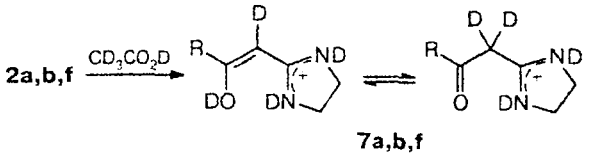


Fig. 2. Molecular packing of compound **2a** projected along the *c* axis. The molecules are linked in chains through intermolecular N(2)—H(N(2))...O(1) hydrogen bonds.

Immediately after the addition of deuteroacetic acid, the signals for the vinyl proton and the protons of the NH groups disappeared and the multiplets for the CH_2 groups coalesced into a singlet at δ 3.82, which is indicative of rapid H/D exchange due to keto-enol tautomerism in the acetonyl substituent[15,16,18,24] and the formation of the symmetrically delocalized imidazolinium monocation **7a**. An analogous situation was also observed for imidazolidines **2b,f**.

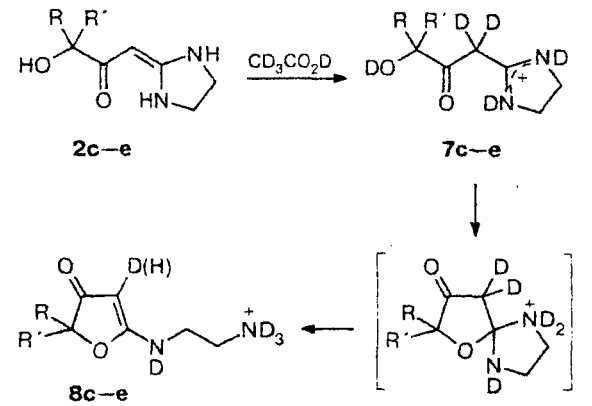
Scheme 4



R = Bu^t (**a**); cyclohexyl (**b**); $Me_2C(OH)CH_2$ (**f**)

However, addition of CD_3CO_2D led to the appearance of two sets of signals in the ^1H NMR spectra of compounds **2c—e** containing the hydroxy group at the α position with respect to the carbonyl group. These sets belong to the expected imidazolinium cations **7** and dihydrofuranones **8** containing the (2-aminoethyl)amino group at position 5 of the ring, respectively. It should be noted that the degrees of conversions **2c** → **8c** and **2d** → **8d** were 25 and 10%, respectively, whereas imidazolidine **2e** (R′ = Bu^t) was recyclized to dihydrofuranone **8e** almost completely (92%) in this time. However, the addition of a solution of CF_3CO_2D in CCl_4 to a solution of compound **2e** in chloroform afforded only cation **7e**.

Scheme 5



R = Me; R′ = Me (**c**); Et (**d**); Bu^t (**e**)

It is most likely that recyclization **2** → **8** proceeded through a spirocyclic intermediate, which was rapidly converted into dihydrofuranone **8** and, consequently, was not detected by ^1H NMR spectroscopy. Conversion **2** → **8** was observed due to the appearance of the A_2X_2 system of protons of the ethylene group and the downfield shifts of the signals of the alkyl substituents by 0.05—0.09 ppm (see the Experimental section). In addition, a

singlet with an intensity of 0.2—0.3 H is observed at δ 4.72—4.74; this signal was absent in the ^{1}H NMR spectra of compounds **2a,b** recorded after addition of CD_3CO_2D, which allows one to assign the signal to the vinyl proton of the dihydrofuranone ring, which had no time to be replaced by deuterium.

Therefore, the reactions of β-amino-β-(trichloromethyl)vinyl ketones **1a—f** with EDA afforded imidazolidines **2a—f**, which have keto-enamine structures and exhibit pronounced basic properties.

Experimental

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

Aminoenones **1a,c,d,f** were described in Refs. 7—9. Compounds **1b,e** were prepared analogously.

Crystals of compound **2a** ($C_9H_{16}N_2O$) are monoclinic. At 20 °C, a = 9.144(2) Å, b = 11.130(2) Å, c = 9.622(2) Å, β = 94.04(2)°, V = 976.9(3) Å^3, d_{calc} = 1.144 g cm^{-3}, the absorption coefficient μ = 0.08 mm^{-1}, space group $P2_1/c$, Z = 4. Intensities of 1354 independent reflections (R_{int} = 0.11) were measured on a four-circle automated Siemens P3/PC diffractometer (Mo-Kα radiation, λ = 0.7107 Å, graphite monochromator, ω scanning technique, $2\theta_{max}$ = 46°).

The structure was solved by the direct method using the SHELXTL-Plus 4.2 and SHELXTL-Plus 5.0 program packages.[25,26] The nonhydrogen atoms were refined isotropically by the full-matrix least-squares method (based on F_0^2). The positions of the hydrogen atoms were calculated geometrically and were refined using the riding model with fixed C—H (N—H) distances and fixed thermal parameters U = 1.5U_{iso} for the methyl groups and U = 1.2U_{iso} for the remaining groups (U_{iso} are isotropic displacement parameters of the corresponding C and N atoms). Then the position of the H(N(1)) atom was refined without restrictions imposed on its geometric characteristics. It was found that the H(N(1)) atom was attached to the N(1) atom. The final R factors were as follows: R_1 = 0.061 (using 264 reflections with $I > 2\sigma(I)$), wR_2 = 0.10, GOOF = 0.871. The principal bond lengths and bond angles for nonhydrogen atoms are given in Table 1.

2-(Pivaloylmethylene)imidazolidine (2a). Aminoenone **1a** (305 mg, 1.25 mmol) was dissolved in EDA (300 μL, 270 mg, 4.5 mmol) and the reaction mixture was kept at ~20 °C for 1 week. The crystals that precipitated were washed with water and recrystallized from CCl_4. Imidazolidine **2a** was obtained in a yield of 100 mg (48%), m.p. 183—184 °C. Found (%): C, 64.10; H, 9.81; N, 16.66. $C_9H_{16}N_2O$. Calculated (%): C, 64.25; H, 9.59; N, 16.65. IR, ν/cm^{-1}: 3300, 3240, 3150 (NH); 3040 (=CH); 1620 (C=O); 1545 (br, C=C, NH). ^{1}H NMR, δ: 1.12 (s, 9 H, Bu^t); 3.51 (m, 2 H, CH_2); 3.67 (m, 2 H, CH_2); 4.83 (br.s, 1 H, NH); 4.89 (s, 1 H, =CH); 9.34 (br.s, 1 H, NH...C=O). Immediately after addition of CD_3CO_2D: **7a**, 1.13 (s, 9 H, Bu^t); 3.82 (s, 4 H, CH_2CH_2).

A mixture was isolated from the mother liquor in a yield of 75 mg. The mixture contained 35% of imidazolidine **2a** and 65% of aminal **3a**. The latter was not isolated in individual form but its structure can be judged from the ^{1}H NMR spectrum of the mixture. ^{1}H NMR, δ: **3a**, 1.13 (s, 9 H, Bu^t); 2.92 (t, 2 H, CH_2, J = 5.2 Hz); 3.21 (m, 2 H, CH_2); 4.74 (s, 1 H, =CH); 5.5 (br.s, 2 H, $\underline{NH_2}$—CH=); 11.3 (br.s, 1 H, NH...O=C). Compounds **2b—f** were prepared analogously to imidazolidine **2a**.

2-(Cyclohexylcarbonylmethylene)imidazolidine (2b). The yield was 50%, m.p. 162—163 °C. Found (%): C, 67.69; H, 9.36; N, 14.50. $C_{11}H_{18}N_2O$. Calculated (%): C, 68.01; H, 9.34; N, 14.42. IR, ν/cm^{-1}: 3310, 3230, 3140 (NH); 1620 (C=O); 1545 (br, C=C, NH). ^{1}H NMR, δ: 1.1—1.8 (m, 10 H, cyclohexyl); 2.1 (m, 1 H, CH of cyclohexyl); 3.51 (m, 2 H, CH_2); 3.67 (m, 2 H, CH_2); 4.55 (br.s, 1 H, NH); 4.72 (s, 1 H, =CH); 9.30 (br.s, 1 H, NH...C=O). Immediately after addition of CD_3CO_2D: **7b**, 1.1—1.8 (m, 10 H, cyclohexyl); 2.3 (m, 1 H, CH of cyclohexyl); 3.80 (s, 4 H, CH_2CH_2).

2-[(1-Hydroxy-1-methylethyl)carbonylmethylene]imidazolidine (2c). The yield was 25%, m.p. 132—133 °C. Found (%): C, 56.44; H, 8.26; N, 16.27. $C_8H_{14}N_2O_2$. Calculated (%): C, 56.45; H, 8.29; N, 16.46. IR, ν/cm^{-1}: 3420, 3360, 3210 (OH, NH); 1615 (C=O); 1560 (C=C, NH). ^{1}H NMR, δ: 1.33 (s, 6 H, 2 Me); 3.58 (m, 2 H, CH_2); 3.72 (m, 2 H, CH_2); 4.77 (s, 1 H, =CH); 4.80 (br.s, 1 H, NH); 5.06 (s, 1 H, OH); 8.89 (s, 1 H, NH...O=C). Immediately after addition of CD_3CO_2D: **7c**, 1.35 (s, 6 H, 2 Me); 3.81 (s, 4 H, CH_2CH_2) (75%); **8c**, 1.42 (s, 6 H, 2 Me); 3.22 (t, 2 H, CH_2—ND_3^+, J = 5.4 Hz); 3.62 (t, 2 H, CH_2—ND, J = 5.4 Hz); 4.72 (s, 0.2 H, =CH) (25%).

2-[(1-Hydroxy-1-methylpropyl)carbonylmethylene]imidazolidine (2d). The yield was 32%, m.p. 142—143 °C. Found (%): C, 58.35; H, 8.66; N, 15.06. $C_9H_{16}N_2O_2$. Calculated (%): C, 58.67; H, 8.75; N, 15.21. IR, ν/cm^{-1}: 3380, 3270, 3220 (OH, NH); 1615 (C=O); 1560 (C=C, NH). ^{1}H NMR, δ: 0.83 (t, 3 H, Me, J = 7.3 Hz); 1.29 (s, 3 H, Me); 1.62 (AB portion of the ABX_3 system, 2 H, $\underline{CH_2}$Me); 3.57 (m, 2 H, CH_2); 3.72 (m, 2 H, CH_2); 4.73 (s, 1 H, =CH); 4.81 (br.s, 1 H, NH); 4.89 (br.s, 1 H, OH); 8.87 (br.s, 1 H, NH...O=C). Immediately after addition of CD_3CO_2D: **7d**, 0.82 (t, 3 H, Me, J = 7.3 Hz); 1.28 (s, 3 H, Me); 1.62 (q, 2 H, $\underline{CH_2}$Me, J = 7.3 Hz); 3.69 (s, 4 H, CH_2CH_2) (90%); **8d**, 0.82 (t, 3 H, Me, J = 7.3 Hz); 1.37 (s, 3 H, Me); 1.75 (m, 2 H, $\underline{CH_2}$Me); 3.18 (t, 2 H, CH_2, J = 5.4 Hz); 3.59 (t, 2 H, CH_2, J = 5.4 Hz); 4.74 (s, 0.3 H, =CH) (10%).

2-[(1-Hydroxy-1,2,2-trimethylpropyl)carbonylmethylene]imidazolidine (2e). The yield was 18%, m.p. 155—156 °C. Found (%): C, 61.97; H, 9.23; N, 12.92. $C_{11}H_{20}N_2O_2$. Calculated (%): C, 62.24; H, 9.50; N, 13.20. IR, ν/cm^{-1}: 3400, 3270, 3230, 3180 (OH, NH); 1620 (C=O); 1570 (C=C, NH). ^{1}H NMR, δ: 0.94 (s, 9 H, Bu^t); 1.28 (s, 3 H, Me); 3.57 (m, 2 H, CH_2); 3.71 (m, 2 H, CH_2); 4.74 (s, 1 H, =CH); 4.80 (s, 1 H, NH); 5.04 (s, 1 H, OH); 8.99 (s, 1 H, NH...O=C). Immediately after addition of CD_3CO_2D: **7e**, 0.93 (s, 9 H, Bu^t); 1.28 (s, 3 H, Me); 3.71 (s, 4 H, CH_2CH_2) (8%); **8e**, 0.98 (s, 9 H, Bu^t); 1.37 (s, 3 H, Me); 3.17 (t, 2 H, $CH_2ND_3^+$, J = 5.2 Hz); 3.57 (t, 2 H, CH_2—ND, J = 5.2 Hz); 4.73 (s, 0.2 H, =CH) (92%). Immediately after addition of CF_3CO_2D: **7e**, 0.97 (s, 9 H, Bu^t); 1.34 (s, 3 H, Me); 4.03 (s, 4 H, CH_2CH_2).

2-[(2-Hydroxy-2-methylpropyl)carbonylmethylene]imidazolidine (2f). The yield was 15%, m.p. 137—138 °C. Found (%): C, 58.80; H, 8.64; N, 15.08. $C_9H_{16}N_2O_2$. Calculated (%): C, 58.67; H, 8.75; N, 15.21. IR, ν/cm^{-1}: 3330, 3260, 3220 (OH, NH); 1615 (C=O); 1565, 1520 (C=C, NH). ^{1}H NMR, δ: 1.21 (s, 6 H, 2 Me); 2.29 (s, 2 H, CH_2); 3.56 (m, 2 H, CH_2); 3.71 (m, 2 H, CH_2); 4.67 (s, 1 H, =CH); 4.89 (s, 1 H, NH); 6.01 (br.s, 1 H, OH); 9.23 (br.s, 1 H, NH...O=C). Immediately after addition of CD_3CO_2D: **7f**, 1.26 (s, 6 H, 2 Me); 2.54 (s, 2 H, CH_2); 3.81 (s, 4 H, CH_2CH_2).

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