Formation of 3-pyrrolin-2-one or imidazolidine derivatives by slow dimerization of *N*-substituted aziridine-2-carboxylates*

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Prolonged storage (45—60 days) of *N*-methyl- or *N*-cyclopropylaziridine-2-carboxylates leads to their dimerization through the N—C(3) bond cleavage to form 1,3-disubstituted 2-methylimidazolidine-2,4-dicarboxylates in high yields. Prolonged storage of 1-benzylaziridine-2-carboxylate (like the reactions of alkyl pyruvates with primary amines) results in cyclocondensation to yield 3-pyrrolin-2-one derivative.

Key words: aziridine-2-carboxylates, imidazolidine-2,4-dicarboxylates, 3-amino-3-pyrrolin-2-ones, isomerization, condensation.

Many aziridines are reactive compounds, which can be involved in addition reactions with either retention or opening of the three-membered heterocycle.[1—3] Among the latter processes, reactions accompanied by the formation of new carbon—carbon bonds occupy a special place. Under thermolysis conditions, *N*-alkyl- and *N*-arylaziridines containing one or two stabilizing groups in the heterocycle (for example, the ester or phenyl substituents) are subjected to electrocyclic opening of the three-membered ring through the intermediate formation of azomethine ylides, which can undergo 1,3-dipolar cycloaddition with olefins or acetylenes to give substituted pyrrolidines or pyrroles.[3—5] These reactions are generally accompanied by selective cleavage of the C(2)—C(3) bond in the aziridine ring, and the formation of five-membered heterocycles occurs with high regio- and stereoselectivity. Unlike these reactions, the addition of C-nucleophiles (in particular, of malonic acid derivatives) to *N*-activated (COPh) or inactivated (CH_2Ph) 2-alkoxycarbonyl- or 2-cyanoaziridines proceeds through cleavage of the N(1)—C(2) and N(1)—C(3) bonds in the aziridine ring.[6—8] In some cases, the resulting functionalized amines undergo cyclization to give the corresponding 2-pyrrolidones due to interaction with the alkoxycarbonyl group in the γ position. Isomerization of aziridines containing conjugated double bonds, including heteroatomic bonds, also affords five-membered heterocycles.[2] However, in spite of the wide use of aziridine-2-carboxylic acid derivatives in various chemical transformations and the detailed study of these compounds by ^1H and ^{13}C NMR spectroscopy,[9] no mention has been made of spontaneous dimerization or condensation of these compounds accompanied by the transformation of the three-membered nitrogen heterocycle into the five-membered ring.

In the present study, we demonstrated, for the first time, that *N*-substituted 2-aziridinecarboxylates **1a—c** are slowly transformed into five-membered nitrogen heterocycles under kinetically controlled conditions (5—20 °C, 45—60 days) as a result of the reaction of two molecules of the starting aziridines.

For example, 1-benzyl-2-aziridinecarboxylate **1a** is virtually completely transformed into 1-benzyl-3-benzylamino-5-ethoxycarbonyl-5-methyl-3-pyrrolin-2-one (**2a**) upon storage at 10 °C for 45—50 days in the absence of a solvent. The starting aziridine **1a** was prepared according to a standard procedure[10] by the reaction of ethyl 2,3-dibromopropionate with benzylamine and then distilled at 95—97 °C (0.2 Torr). Apparently, pyrrolin-2-one **2a** is formed due to slow isomerization of aziridine **1a**, involving the N(1)—C(3) bond cleavage to give a tautomeric mixture of imine **3a** and enamine **4a** followed by their cyclocondensation (Scheme 1). This interpretation is consistent with the results of the reaction of methyl pyruvate with benzylamine, which has been described earlier[11] and proceeds, presumably, through the intermediate formation of the corresponding imine and enamine, as well as with our data on the synthesis of pyrrolin-2-one **2a** by the reaction of ethyl pyruvate with benzylamine.

The reaction of pyrrolinone **2a** with semicarbazide hydrochloride in aqueous EtOH in the presence of AcONa results in hydrolysis of the enamine fragment and the formation of crystalline semicarbazone **5** (see Scheme 1).

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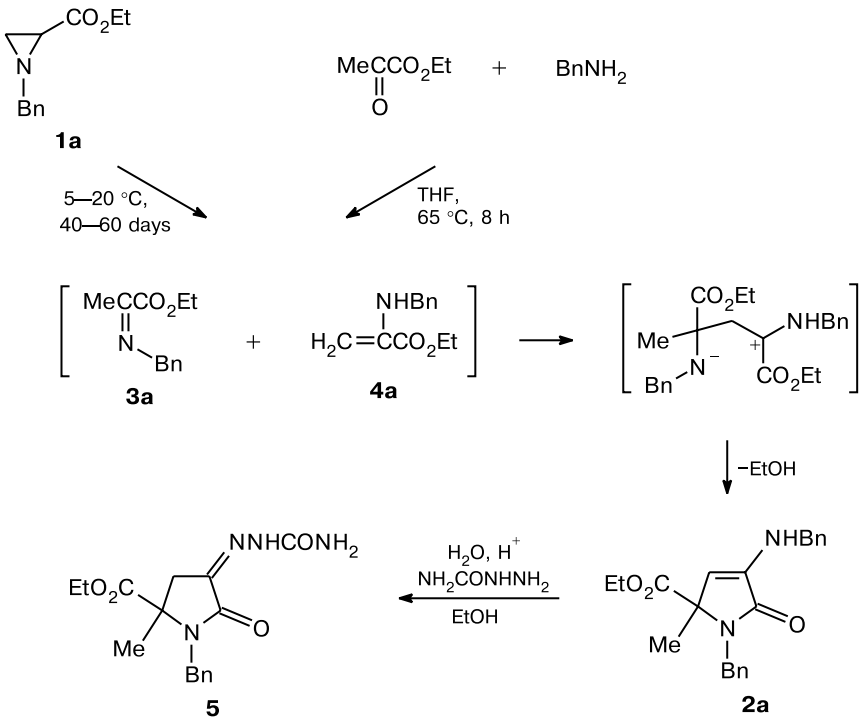
Scheme 1



The structure of the latter was unambiguously established by X-ray diffraction analysis.

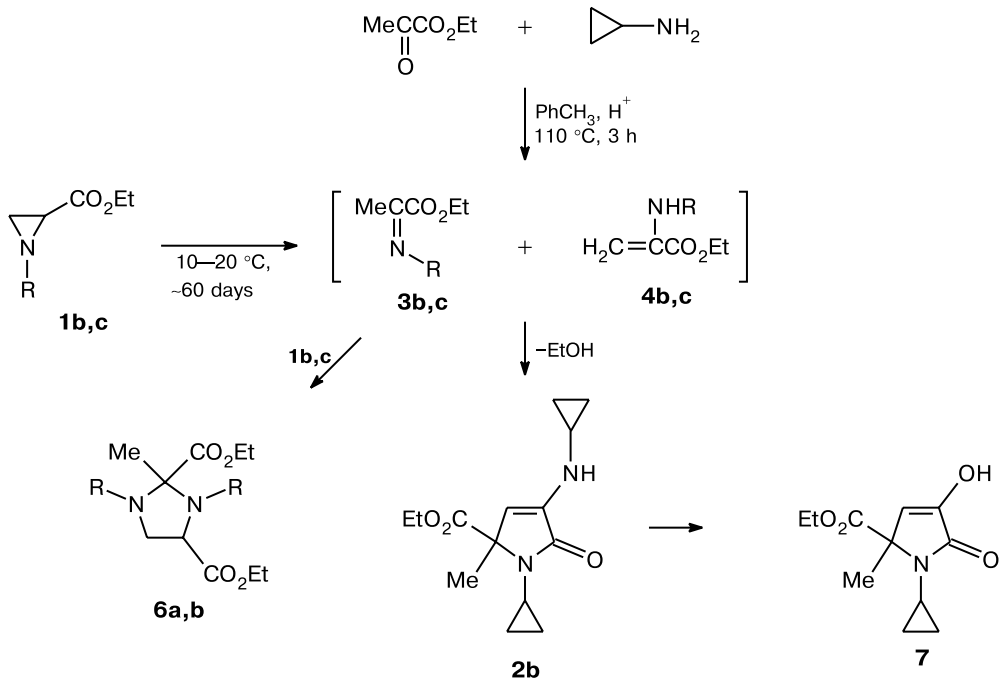
Interestingly, the transformation of ethyl 1-cyclopropylaziridine-2-carboxylate **1b**, which we synthesized for the first time, proceeds by a different mechanism. Prolonged storage (~2 months) of aziridine **1b** at 20 °C in the absence of a solvent leads to dimerization, without elimination of EtOH, to give 1,3-dicyclopropyl-2,4-bis(ethoxycarbonyl)-2-methylimidazolidine (**6a**) in a yield as high as 98% (Scheme 2). 1-Methylaziridinecarboxylate **1c** undergoes analogous isomerization, but the reaction is less selective and gives (^{1}H NMR spectrum of the reaction mixture) imidazolidine **6b** in ~80% yield, 10—12% of the starting aziridinecarboxylate **1c** remaining unconsumed. Analysis of the ^{1}H and ^{13}C NMR spectra demonstrated that imidazolidine-2,4-dicarboxylates **6a,b** are produced as a mixture of *cis* and *trans* isomers in a ratio of 1 : (1.8—2). Storage of aziridine **1c** over a longer period of time (10 °C, 6 months) leads to its almost complete conversion, but the ratio of the *cis* to *trans* isomers changes to 1 : 4.

The formation of imidazolidine derivatives in these reactions also proceeds, apparently, through isomerization of aziridines **1b,c** to yield reactive imines **3b** or **3c**. However, the latter undergo *C,N*-coupling directly with aziridines **1b,c**, unlike benzyl derivatives, which undergo *C,C*-coupling with isomeric enamines **4b** or **4c**. This fact is, apparently, attributable to the higher nucleophilicity of the nitrogen atom of the starting aziridines **1b,c** compared to **1a**. We found that the reaction of ethyl pyruvate with cyclopropylamine in refluxing toluene in the presence of catalytic amounts of TsOH (~10 h) proceeds analogously to the reaction of benzylamine and produces cyclopropyl-substituted 3-pyrrolin-2-one **2b** in 81% yield. The reaction is accompanied by partial hydrolysis of 3-benzylamino-substituted 3-pyrrolin-2-one **2b** to give 3-hydroxy-3-pyrrolin-2-one **7** as a by-product (~9%) (see Scheme 2).

When the reaction was terminated after ~3 h, imine **3b** was obtained as the major product, which was confirmed by the ^{1}H NMR spectra showing a signal for the protons of the Me—C=N fragment at δ 2.21 (**2b** : **3b** : **7** = 5 : 7.5 : 1). Therefore, in spite of the fact that both reactions (either isomerization of aziridine **1b** or condensation of ethyl pyruvate with cyclopropylamine) can produce the same imine **3b**, its further transformations depend on the nature of the nucleophilic substrate. Either aziridine (in the case under consideration, cyclopropylaziridine **1b**) or enamine **4b**, which exists apparently in tautomeric equilibrium with imine **3b**, can serve as such a substrate.

Unlike aziridinecarboxylates **1a—c**, 1-benzyl-2-aziridinecarbonitrile (**8**), which has similar properties and exists as a mixture of *trans* and *cis* isomers, does not give cyclodimerization products analogous to heterocyclic structures **2** or **6**. This difference is, apparently, associated, on the one hand, with a lower reactivity of isomeric

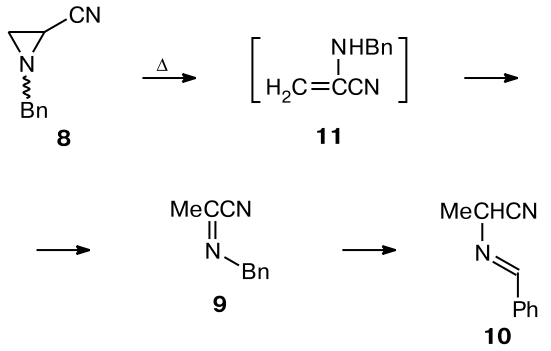
Scheme 2



1—4: R = *cyclo*-C_3H_5 (**b**), Me (**c**); **6:** R = *cyclo*-C_3H_5 (**a**), Me (**b**)

1-benzyl-2-iminopropionitrile (**9**), due to which it can be observed in the isomerization of aziridinecarbonitrile **8**, and, on the other hand, with the fact that compound **9** is readily isomerized into stable *N*-benzylidene-2-aminopropionitrile (**10**) (Scheme 3).[12] Neither thermal isomerization of isomeric aziridines **8** nor storage of these compounds in a mixture with imine **9** was accompanied by the formation of enamine **11** and, consequently, cyclodimerization products.

Scheme 3



To summarize, prolonged storage of aziridine-2-carboxylates under usual conditions leads to slow isomerization giving rise to a tautomeric mixture of imines **3a—c** and enamines **4a—c** accompanied by the N—C(3) bond cleavage. The reactions of 1-methyl- or 1-cyclopropylaziridine-2-carboxylates **1b,c** produce 1,3-disubstituted 2-methylimidazolidine-2,4-dicarboxylates **6a,b** in high yields, whereas the reaction of 1-benzylaziridine-2-carboxylate gives 3-pyrrolin-2-one derivative **2a** (like the reactions of alkyl pyruvates with primary amines).

Experimental

The ^1H and ^{13}C NMR spectra were recorded on Bruker AC-200 (200 and 50.3 MHz) and Bruker AM-300 (300 and 75.5 MHz) spectrometers in $CDCl_3$ or DMSO-d_6 containing 0.05% of Me_4Si as the internal standard. The mass spectra were obtained on a Finnigan MAT INCOS-50 instrument (EI, 70 eV, 30 m RSL-200 capillary column or direct inlet). The IR spectra were recorded on a Bruker IFS-113v spectrometer in CCl_4. Ethyl 1-methylaziridine-2-carboxylate and ethyl 1-benzylaziridine-2-carboxylate (**1a,c**) were prepared according to known procedures.[10,13] The ^{13}C NMR spectrum of compound **1c** (δ): 14.1 (Me); 35.7 (C(3)); 38.4 (C(2)); 47.1 (Me—N); 61.0 (OCH_2); 170.9 (C=O).

Ethyl 1-cyclopropylaziridine-2-carboxylate (1b) was synthesized analogously to aziridines **1a,c** from ethyl 2,3-dibromopropionate (4.42 g, 17 mmol), cyclopropylamine (0.97 g, 17 mmol), and NEt_3 (3.44 g, 34 mmol) in MeCN (75 mL) for 2 days. Aziridine **1b** was obtained in a yield of 1.74 g (66%) as a colorless liquid, b.p. 71.5—73.5 °C (1 Torr). Found (%): C, 61.78; H, 8.40; N, 8.97. $C_8H_{13}NO_2$. Calculated (%): C, 61.91; H, 8,44; N, 9.03. IR, ν/cm^{-1}: 3091 (CH of the cyclopropane ring); 3013 (CH of the aziridine ring); 1743 (C=O); 1186, 1060,

1036 (CO). ^{1}H NMR ($CDCl_3$), δ: 0.45 and 0.65 (both m, 2 H each, CH_2CH_2); 1.26 (t, 3 H, Me, ^3J = 7.0 Hz); 1.48 (tt, 1 H, CH in *cyclo*-C_3H_5, J_{cis} = 6.9 Hz, J_{trans} = 3.4 Hz); 1.80 (dd, 1 H, H_a(3), ^2J = 1.3 Hz, J_{cis} = 6.5 Hz); 2.15 (dd, 1 H, H_b(3), ^2J = 1.3 Hz, J_{trans} = 3.1 Hz); 2.25 (dd, 1 H, H(2), J_{cis} = 6.5 Hz, J_{trans} = 3.1 Hz); 4.20 (m, 2 H, OCH_2). ^{13}C NMR ($CDCl_3$), δ: 4.8 and 5.0 (CH_2CH_2); 13.9 (Me); 33.8 (C(3)); 36.7 (C(2)); 40.4 (CH in *cyclo*-C_3H_5); 60.8 (OCH_2); 170.6 (C=O). Partial mass spectrum, *m/z* (I_{rel} (%)): 126 $[M - Et]^+$ (30), 110 (5), 96 (20), 82 (65), 55 (100), 40 (60).

1-Benzyl-3-benzylamino-5-ethoxycarbonyl-5-methyl-3-pyrrolin-2-one (2a). Ethyl aziridinecarboxylate **1a** (6.16 g, 0.03 mol) was kept in the absence of solvents at 10 °C for 50 days. After removal of the ethanol that formed *in vacuo*, pyrrolinone **2a** was obtained in a yield of 5.47 g (~100%) as a weakly colored viscous liquid in individual form (TLC data). Found (%): C, 72.44; H, 6.66; N, 7.62. $C_{22}H_{24}N_2O_3$. Calculated (%): C, 72.51; H, 6.64; N, 7.69. IR, ν/cm^{-1}: 3400—3200 (NH); 1732 (COO); 1695 (NCO); 1658 (C=C). ^{1}H NMR ($CDCl_3$), δ: 1.10 (t, 3 H, OCH_2Me, ^3J = 7.0 Hz); 1.35 (s, 3 H, Me); 3.90 (m, 2 H, OCH_2); 4.20 (d, 2 H, NCH_2, ^3J = 5.5 Hz); 4.65 (t, 1 H, NH, ^3J = 5.5 Hz); 4.35 and 4.85 (both d, 1 H each, CH_2—N(1), ^2J = 15.2 Hz); 5.15 (s, 1 H, H(4)); 7.25 (m, 10 H, Ph). ^{13}C NMR ($CDCl_3$), δ: 13.6 (OCH_2Me); 21.3 (Me); 44.3 (NCH_2); 47.9 ($NHCH_2$); 61.1 (OCH_2); 67.1 (C(5)); 103.7 (C(4)); 127.0, 127.7, 128.0, 128.1, 128.2 (CH of benzene rings); 137.7 and 137.3 (C_{ipso} of benzene rings); 139.5 (C(3)); 167.8 (C(2)); 171.2 (COO). Partial mass spectrum, *m/z* (I_{rel} (%)): 364 $[M]^+$ (60), 291 (43), 91 (100).

1-Benzyl-5-ethoxycarbonyl-5-methylpyrrolidine-2,3-dione 3-semicarbazone (5). The reaction of pyrrolinone **2a** (0.98 g, 2.7 mmol) and semicarbazide hydrochloride (0.30 g, 2.7 mmol) in the presence of AcONa · $3H_2O$ (0.50 g, 3.7 mmol) in aqueous EtOH produced semicarbazone **5** in a yield of 0.48 g (54%), m.p. 211—212 °C (from 30% aqueous EtOH). Found (%): C, 57.78; H, 6.05; N, 16.81. $C_{16}H_{20}N_4O_4$. Calculated (%): C, 57.82; H, 6,07; N, 16,86. ^{1}H NMR (DMSO-d_6), δ: 1.05 (t, 3 H, OCH_2Me, ^3J = 7.0 Hz); 1.45 (s, 3 H, Me); 2.65 and 3.15 (both d, 1 H each, CH_2, ^2J = 18.5 Hz); 3.85 (m, 2 H, OCH_2); 4.40 and 4.59 (both d, 1 H each, NCH_2Ph, ^2J = 15.5 Hz); 6.50 (br.s, 2 H, NH_2); 7.25 (m, 5 H, Ph); 9.80 (s, 1 H, NH). ^{13}C NMR (DMSO-d_6), δ: 13.15 (OCH_2Me); 21.8 (Me); 35.3 (C(4)); 43.6 (NCH_2); 61.0 (C(5)); 61.7 (OCH_2); 126.6 (*p*-CH); 127.2, 127.7 (*o*-CH, *m*-CH); 136.8 (C_{ipso}); 138.8 (C(3)); 156.0 ($CONH_2$); 164.1 (NC=O); 171.6 (COO). Partial mass spectrum, *m/z* (I_{rel} (%)): 332 $[M]^+$ (5), 288 $[M-NH_2CO]^+$ (5), 273 $[M - NH_2CONH]^+$ (3), 259 $[M - CO_2Et]^+$ (15), 242 (20), 216 (20), 91 (100).

Diethyl 1,3-dicyclopropyl-2-methylimidazolidine-2,4-dicarboxylate (6a). Ethyl 1-cyclopropylaziridine-2-carboxylate (**1b**) (0.93 g, 6 mmol) was kept without a solvent at 20 °C for 60 days. The liquid remained colorless but became more viscous than the starting ester **1b**. The product was additionally kept *in vacuo* at 70 °C (0.5 Torr) for 15 min, after which the weight loss was 0.02 g. The ^{1}H and ^{13}C NMR spectra showed that the product was a mixture of two isomeric imidazolidine-2,4-dicarboxylates **6a** (*trans* : *cis* ≈ 1.8 : 1). Found (%): C, 61.96; H, 8.49; N, 9.00. $C_{16}H_{26}N_2O_4$. Calculated (%): C, 61.91; H, 8.44; N, 9.03. IR, ν/cm^{-1}: 3091 (CH of the cyclopropane ring), 1749 and 1733 (C=O). Partial mass spectrum, *m/z* (I_{rel} (%)): 310 $[M]^+$ (2), 237 $[M - CO_2Et]^+$ (100), 209 (30), 156 (25), 126 (30), 82 (45), 55 (25), 41 (90).

Compound *trans*-**6a**. ^{1}H NMR ($CDCl_3$), δ: 0.25—0.70 (m, 2 CH_2CH_2); 1.25 and 1.30 (both t, 2 OCH_2Me, ^3J = 7.0 Hz); 1.55 (s, Me); 1.72 and 1.90 (both m, 2 CHN); 3.07 (dd, H_aC(5), ^3J = 3.8 Hz, ^2J = 9.0 Hz); 3.46 (t, H_bC(5), ^2J = ^3J = 9.0 Hz); 3.90 (dd, H(4), ^3J = 3.8 Hz, ^3J = 9.0 Hz); 4.05—4.25 (m, 2 OCH_2). ^{13}C NMR ($CDCl_3$), δ: 4.1, 4.5, 6.7, and 7.2 (2 CH_2CH_2); 14.2 and 14.7 (2 OCH_2Me); 21.5 (Me); 29.3 and 29.6 (2 CHN); 54.8 (C(5)); 60.3 and 60.7 (2 OCH_2); 63.5 (C(4)); 85.2 (C(2)); 172.6 and 174.6 (2 COO).

Compound *cis*-**6a**. ^{1}H NMR ($CDCl_3$), δ: 0.25—0.70 (m, 2 CH_2CH_2); 1.15 and 1.20 (both t, 2 OCH_2Me, ^3J = 7.0 Hz); 1.60 (s, Me); 1.92 and 2.21 (both m, 2 CHN); 3.32 (dd, H_aC(5), ^3J = 3.5 Hz, ^2J = 8.0 Hz); 3.80 (t, H_bC(5), ^2J = ^3J = 8.0 Hz); 4.05—4.25 (m, 2 OCH_2 and H(4)). ^{13}C NMR ($CDCl_3$), δ: 6.3, 6.4, 6.7, and 7.7 (2 CH_2CH_2); 14.2 and 14.7 (2 OCH_2Me); 19.7 (Me); 28.6 and 30.9 (2 CHN); 53.9 (C(5)); 60.3 and 60.5 (2 OCH_2); 64.2 (C(4)); 85.2 (C(2)); 173.7 and 174.6 (2 COO).

Diethyl 1,2,3-trimethylimidazolidine-2,4-dicarboxylate (6b). Aziridinecarboxylate **1c** (3.87 g, 0.03 mol) was kept at 18 °C for 60 days and then at 70 °C (0.5 Torr) for 15 min, after which the resulting colorless viscous liquid was analyzed by ^{1}H and ^{13}C NMR spectroscopy. The *trans*- to *cis*-**6b** ratio was ~2 : 1.

Compound *trans*-**6b**. ^{1}H NMR ($CDCl_3$), δ: 1.25 (t, 2 OCH_2Me, ^3J = 7.0 Hz); 1.40 (s, 3 H, Me); 2.27 and 2.39 (both s, 2 NMe); 3.18 (dd, H_bC(5), ^3J = 10.1 Hz, ^2J = 8.8 Hz); 3.31 (dd, H_aC(5), ^3J = 3.7 Hz, ^2J = 8.8 Hz); 3.65 (dd, H(4), ^3J = 10.1 Hz, ^3J = 3.7 Hz); 4.10—4.30 (m, 2 OCH_2). ^{13}C NMR ($CDCl_3$), δ: 14.0 and 14.6 (2 OCH_2Me); 19.9 (Me); 34.6 and 35.1 (2 NMe); 54.6 (C(5)); 59.7 and 60.6 (2 OCH_2); 63.5 (C(4)); 84.9 (C(2)); 171.0 and 172.7 (2 COO).

Compound *cis*-**6b**. ^{1}H NMR ($CDCl_3$), δ: 1.26 (t, 2 OCH_2Me, ^3J = 7.0 Hz); 1.34 (s, 3 H, Me); 2.34 and 2.54 (both s, 2 NMe); 3.14 (dd, H_aC(5), ^3J = 7.8 Hz, ^2J = 8.5 Hz); 3.28 (dd, H_bC(5), ^3J = 7.5 Hz, ^2J = 8.5 Hz); 3.60 (dd, H(4), ^3J = 7.5 Hz, ^3J = 7.8 Hz); 4.13—4.33 (m, 2 OCH_2). ^{13}C NMR ($CDCl_3$), δ: 13.8 and 14.1 (2 OCH_2Me); 16.9 (Me); 34.9 and 35.9 (2 NMe); 54.2 (C(5)); 60.6 and 61.4 (2 OCH_2); 64.6 (C(4)); 82.7 (C(2)); 171.4 and 171.8 (2 COO). Partial mass spectrum, *m/z* (I_{rel} (%)): 258 $[M]^+$ (55), 185 $[M - CO_2Et]^+$ (100).

Reaction of ethyl pyruvate with cyclopropylamine. A mixture of ethyl pyruvate (0.29 g, 2.5 mmol), cyclopropylamine (0.143 g, 2.5 mmol), and TsOH (0.6 mg) was refluxed in anhydrous toluene for 3 h. A small sample was withdrawn, the solvent was removed *in vacuo*, and the ^{1}H NMR spectrum was recorded, which demonstrated that the reaction mixture consisted of ethyl 2-(cyclopropylimino)propionate (**3b**), 1-cyclopropyl-3-cyclopropylamino-5-ethoxycarbonyl-5-methyl-3-pyrrolin-2-one (**2b**), and 1-cyclopropyl-5-ethoxycarbonyl-3-hydroxy-5-methyl-3-pyrrolin-2-one (**7**) in a molar ratio of ~7.5 : 5 : 1. Then the mixture was refluxed for 7 h, after which the ^{1}H NMR spectrum showed only signals of 3-pyrrolin-2-one **2b** and 3-hydroxy-3-pyrrolin-2-one **7** (~9 : 1 ratio). Both compounds were isolated by preparative TLC on SiO_2 (diethyl ether—hexane, 2 : 1, as the eluent).

Pyrrolinone **2b**. The yield was 81%, colorless oil, R_f 0.51. Found (%): C, 63.86; H, 7.74; N, 10.43. $C_{14}H_{20}N_2O_3$. Calculated (%): C, 63.62; H, 7.63; N, 10.60. IR, ν/cm^{-1}: 3324 (NH); 3093 (CH); 1733 (COO); 1699 (C=O); 1658 (C=C). ^{1}H NMR

($CDCl_3$), δ: 0.50, 0.65, and 0.72—0.90 (all m, 2 H, 2 H and 4 H, 2 CH_2CH_2); 1.25 (t, 3 H, OCH_2Me, ^3J = 7.0 Hz); 1.63 (s, 3 H, Me); 2.35 and 2.50 (both m, 1 H both, CH in *cyclo*-C_3H_5); 4.05—4.25 (m, 2 H, OCH_2); 4.50 (br.s, 1 H, NH); 5.30 (s, 1 H, =CH). ^{13}C NMR (DMSO-d_6), δ: 3.6, 5.6, 6.2, and 6.3 (2 CH_2CH_2); 13.9 (OCH_2Me); 21.2 (Me); 23.0 and 24.8 (2 CH in *cyclo*-C_3H_5); 61.5 (OCH_2); 68.0 (C(5)); 104.9 (C(4)); 140.4 (C(3)); 169.1 (C(2)); 172.3 (COO). Partial mass spectrum, *m/z* (I_{rel} (%)): 264 $[M]^+$ (25), 191 $[M - COOEt]^+$ (100), 164 (40), 156 (30), 136 (30), 82 (50), 41 (70).

Pyrrolinone **7**. The yield was 9%, the purity was ~95%, oil, R_f 0.83. IR, ν/cm^{-1}: 3372 (OH); 3093 (CH); 1774 (C=O); 1738 (COO); 1662 (C=C). ^{1}H NMR ($CDCl_3$), δ: 0.55 and 0.68 (both m, 2 H each, CH_2CH_2); 1.30 (t, 3 H, OCH_2Me, ^3J = 7.0 Hz); 1.71 (s, 3 H, Me); 2.40 (m, 1 H, CH in *cyclo*-C_3H_5); 4.21 (q, 2 H, OCH_2, ^3J = 7.0 Hz); 4.35 (br.s, 1 H, OH); 5.82 (s, 1 H, =CH). ^{13}C NMR ($CDCl_3$), δ: 6.7 (CH_2CH_2); 14.1 (OCH_2Me); 23.5 (Me); 25.5 (CH in *cyclo*-C_3H_5); 62.2 (OCH_2); 84.5 (C(5)); 111.2 (C(4)); 135.7 (C(3)); 169.6 (C(2)); 170.1 (COO). Partial mass spectrum, *m/z* (I_{rel} (%)): 225 $[M]^+$ (15), 152 $[M - COOEt]^+$ (100), 124 (30), 82 (30), 43 (60), 41 (55).

Compound **3b**. ^{1}H NMR ($CDCl_3$), δ: 1.02—1.13 (m, 4 H, CH_2CH_2); 1.29 (t, 3 H, OCH_2Me, ^3J = 7.0 Hz); 2.21 (s, 3 H, Me); 3.05 (m, 1 H, CH in *cyclo*-C_3H_5); 4.30 (m, 2 H, OCH_2, ^3J = 7.0 Hz).

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