REACTIONS OF DIMETHYL 2-METHOXYISOXAZOLIDINE-3,3-DICARBOXYLATE CATALYZED BY LEWIS ACIDS

V. F. Rudchenko, V. N. Voznesenskii, and R. G. Kostyanovskii

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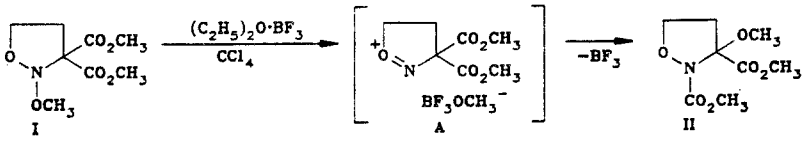
Evidence is presented for a synchronous mechanism of the acid-catalyzed 1,2-rearrangement of 2-methoxyisoxazolidine-2,3-dicarboxylic acid ester with migration of the ester group to the N atom. It was shown that the reaction is suppressed in the presence of an external nucleophile or a reducing agent. The regularities found were used to explain the transformations of bicyclic systems with an –ONO– fragment.

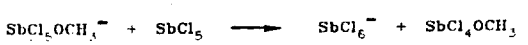
The most characteristic property of compounds with an –ONO– fragment, in particular of 2-alkoxyisoxazolidines, is their tendency to undergo electrophilic reactions [1, 2]. The electrophilic attack on one of the oxygen atoms leads to weakening and subsequent splitting of the N–O bond. This process is realized under stereoelectronic control conditions [2, 3] and is accompanied by various transformations. Thus, in the presence of an electrofuge group (H, NO_2, CH_3NHCO) in the N-substituent at the α–C atom, the α,β-elimination predominates [2, 4]. In other cases the following are realized: nucleophilic substitution of the alkoxyl group [1, 2, 5, 6] or the formation of C-nitroso compounds [1] in the presence of an external nucleophile; a one-electronic reduction to azoxy compounds via the stage of formation of alkoxyaminyl radicals or a two-electronic reduction to alkoxyamines in the presence of reducing agents [1]; oxidation to nitro compounds [7] in the presence of an oxidizing agent; 1, 2- [1, 2, 7-9] or 1,3-rearrangements [1] with the migration of groups to the N atom in the absence of the above-enumerated reagents. The mechanism of these reactions was not studied in detail.

An attempt was made in the present work to clarify the mechanism of the 1,2-rearrangement with migration of the carbonyl group to the N atom, which is observed for mono- [2], bi- [8, 9], and acyclic [1, 7] N,N-dialkoxyamines, and also N-chloro-N-alkoxyamines [7, 10] and oxaziridines [12]. For this purpose we studied in detail the previously discovered rearrangement of 2-methoxyisoxazolidine (I) into 3-methoxyisoxazolidine (II) [2]. This reaction was chosen because of the unequivocal occurrence of the rearrangement and the presence of optically active derivatives of isoxazolidine I [12, 13], which makes it possible to observe the stereochemistry of the reaction.



I A II

It was previously assumed [2] that the rearrangement is realized by an ionic mechanism via a delocalized nitrenium ion A, whereby the reaction was carried out in a heterogeneous phase with an equimolar amount of $(C_2H_5)_2O{\cdot}BF_3$ (ETB). We assumed that if the supposition for the ionic reaction mechanism is true, then in reaction of isoxazolidine I in solution with two equivalents of a Lewis acid such as $SbCl_5$, a salt of the nitrenium ion should be obtained generated by the reaction of the nitrenium ion with the weakly nucleophilic anion $SbCl_6^-$ formed during the disproportionation according to the scheme [14]:



This could have been confirmed by the transformation of this salt by the action of methanol in the presence of a base into the initial isoxazolidine I as a result of the addition of a nucleophile to the nitrenium center. It was found that in the reaction

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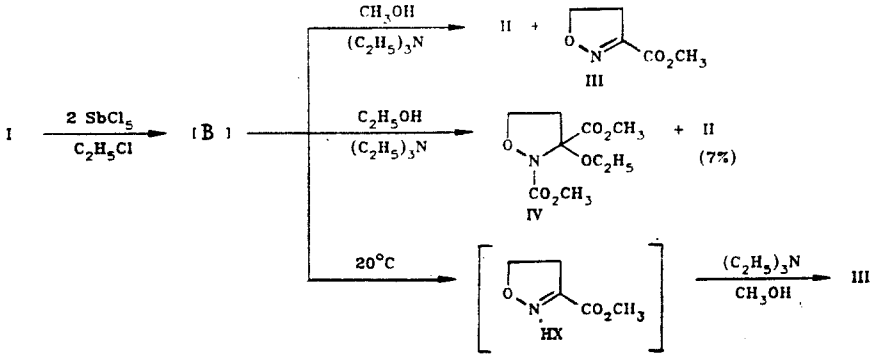
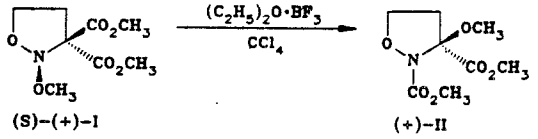
of isoxazolidine I with two equivalents of $SbCl_5$, a saltlike product **B** is formed which, however, in reaction with alcohols, instead of the expected 2-alkoxyisoxazolidines, gives mainly products II and IV. A hygroscopic compounds was obtained in an attempt to isolate compound **B**, possibly being a salt of isoxazoline-3-carboxylic acid ester, which when treated with triethylamine in methanol gave isoxazoline III

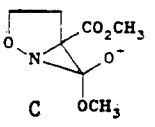


It should be emphasized that isoxazolidine IV is formed directly from the intermediate compound **B** and is not a product of an acid-catalyzed transformation of isoxazolidine II, since it was shown by a special experiment that the latter does not change under the reaction conditions. The data obtained repudiate the previously advanced supposition on the formation of the intermediate **A** during the I → II rearrangement by the action of ETC. Its synchronous mechanism is indicated by the practically complete retention of the optical purity during the rearrangement of the optically active isoxazolidine (s)-(+)-I (preliminary communication, see [15]).

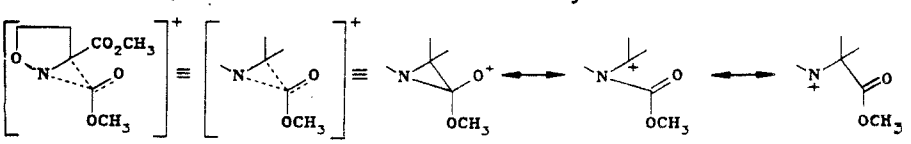


This agrees with the data of the well-investigated 1,2-shift of the carbonyl group to the electron-deficient C atom, which occurs as a concerted process with the inversion of the configuration at the C atom bound to the leaving group [16-18]. According to the ab initio calculations [16, 18], the transition state of the rearrangement is well described by the structure of the cyclopropyloxenium ion. The geometrical requirements with respect to the concerted 1,2-carbonyl migration are as follows [16]: 1) an antiperiplanar disposition of the migrating group with respect to the bond with the leaving group; 2) the atomic p-orbital of the carbonyl π-bond should be parallel to the C–C bond, with respect to which the migration takes place, which is necessary for the formation of Walsh orbitals of the cyclopropane ring.

Isoxazolidine I fully satisfies these requirement, since it exists in the form of an axial anomer [2, 3], whose geometry is favorable for the concerted 1,2-shift of the trans-CH_3O_2C group (relative to the substituent at the N atom). In analogy with the 1,2-carbonyl migration to the C atom, the existence of a cyclic oxenium ion **C** can be assumed – an aza analog of the cyclopropyloxenium ion in the coordinates of the I → II rearrangement by the action of ETC.

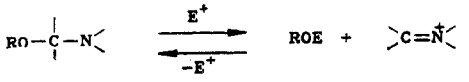


The stereospecific opening of the three-membered ring of this ion by the action of the $BF_3OCH_3^-$ anion present in the reaction mixture leads to the end product. This explains the retention of the optical activity during the rearrangement of isoxazolidine (s)-(+)-I. In this case, the intermediate state **B** in the reaction of isoxazolidine I with $SbCl_5$ can possibly be represented as a salt of the $SbCl_6^-$ anion with a cation, the structure of which is described by canonical structures:

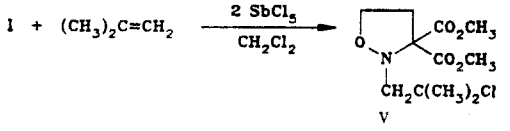


The formation of the α,β-elimination product (isoxazoline III) in the reaction of the intermediate compound **B** with methanol and during its dissociation is due to the contribution of the last structure. The CH_3O_2C group thus acts as an electrofuge.

It should be noted that there are data [8] on the nonstereospecificity of the 1,2-rearrangement with the migration of the acetyl group to the N atom during the ETB initiated transformation of cis-6-acetyl-8-phenyl-2,9-dioxa-1-azabicyclo[4.3.0]nonane into derivatives of spiro-[isoxazolidine-3,2']tetrahydrofuran. It can be assumed, however, that the apparent nonsynchronous character of the rearrangement in this case is due to the subsequent epimerization at the $C_{(3)}$ atom of the isoxazolidine ring as the result of an acid-catalyzed reversible splitting-addition reaction

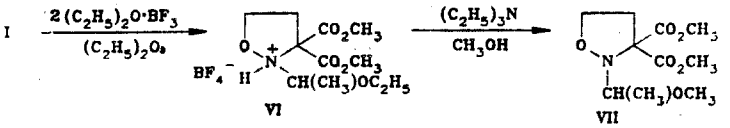


We have also found that the 1,2-shift of the CH_3O_2C group in isoxazolidine I is suppressed in the presence of an external nucleophile – an olefin. Thus, during the treatment of isoxazolidine with isobutylene in the presence of $SbCl_5$ in a CH_2Cl_2 medium, a product of an electrophilic addition to the double bond – compound V – is formed:

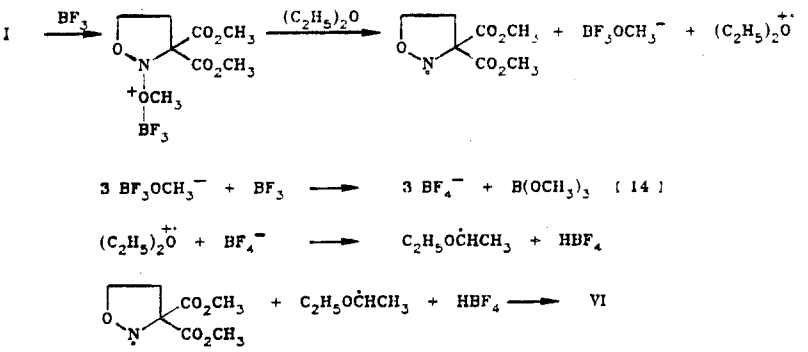


This is completely normal, since the C=C bond is a stronger nucleophile than the carbonyl π-bond. The absence of a 1,2-rearrangement was previously noted in an acid-catalyzed reaction of isoxazolidine I with ethanol [2]. In the presence of methanol the 1,2-shift of the carbonyl group to the carbon atom is also partially or completely suppressed [17].

The reaction of isoxazolidine I with ETB in ether, which leads to the formation of salt VI (identified from the PMR data) occurs unexpectedly. During the isolation of base from salt VI, an acid-catalyzed substitution of the C_2H_5O group takes place with the formation of product VII, which is characteristic for alkoxymethylamines [19]



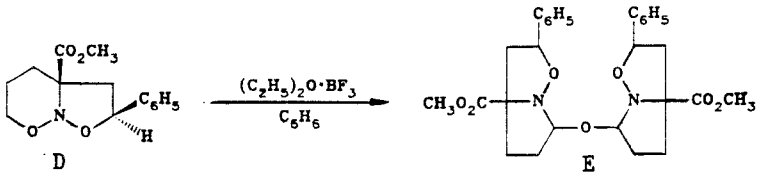
The transformation of compounds I → VI can be explained by a scheme which includes the reductive splitting of the activated exocyclic N–O bond of isoxazolidine I to alkoxyaminyl radical by the action of ether:



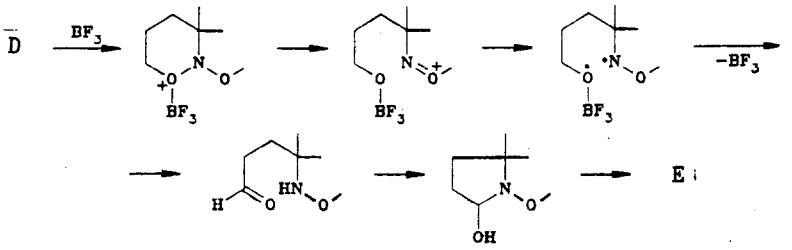
The formation of alkoxyaminyl radicals was previously observed during the reduction of N,N-dialkoxyamines by the action of triethylamine hydrochloride [1], and also in the reactions of N-chloro-N-alkoxyamines with amines [20], a Grignard reagent, sodium ethyl thiolate, and triphenylphosphine [21]. The sterically hindered acyclic alkoxyaminyl radicals were recorded according to the EPR spectra at room temperature [22].

Thus, the 1,2-shift of the carbonyl group in isoxazolidine I is also suppressed in the presence of a reducing reagent.

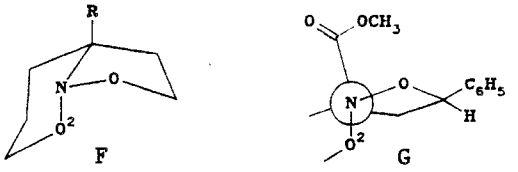
On the basis of these data, the redox mechanism also appears to be probable for the following unusual and previously uninterpreted rearrangement of the bicyclic analog of isoxazolidine I – compound **D** [9].



The proposed reaction scheme includes the BF_3 catalyzed heterolysis of the N–O bond of the six-membered ring with the formation of a stabilized nitrenium ion, its reduction to alkoxyaminyl radical by the action of an internal electron-donor group, disproportionation of the radical pair, and cyclization

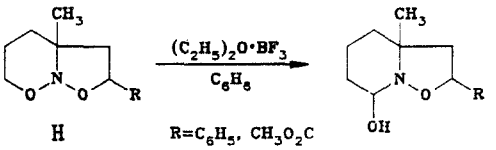


The scheme includes a substantial contradiction – the splitting of the N–O bond is permitted without the anchimeric assistance of the carbonyl group, while, as is known, a bicyclic compound similar to **D**, with the same configuration but with an acetyl group instead of the ester group, under the same conditions, undergoes a 1,2-rearrangement [8]. However, this contradiction is readily explainable if we consider the geometrical requirements for the concerted 1,2-shift of the carbonyl group (see above). It is known [2, 3] that in bicyclic compounds of this type a cis-coupling of rings (**F**) is realized with an antiperiplanar disposition of the rings of the substituent at $C_{(6)}$ and the $N–O_{(2)}$ bond, i.e., the geometry of the bicyclic compound is favorable for a synchronous 1,2-shift of the substituent R to the nitrogen atom. However, for the concerted carbonyl group migration this is insufficient since it is also necessary for the system to acquire a conformation having a perpendicular disposition of the C–C=O plane with respect to the C–N bond. Analysis of molecular models of two such possible conformations of the bicyclic compound **D** shows that conformation **G** (a Newman's projection along the N–C bond) is unfavorable because of steric repulsion between the CH_3O_2C group and the cis-substituent at $C_{(8)}$:



This is probably the reason for the prohibition of the concerted migration in this case, since the rearrangement is readily realized when the CH_3O_2C is replaced by the less bulky acetyl group. The correctness of these considerations is confirmed by the fact that the character of the rearrangements of the derivatives of this bicyclic compound is dependent on the configuration at the $C_{(8)}$ center [9]. The geometry of the bicyclic compound **D**, reflected by structure **F**, is optimal for the $(n\pi_{(O)}–\sigma_{N–O_{(2)}})$ overstrain [2, 3], which also determines the ready acid-catalyzed ionization of the $N–O_{(2)}$ bond with the formation of the corresponding alkoxy nitrenium ion. It should be emphasized that the participation of alkoxynitrenium ions is also assumed in acid-catalyzed transformations of acyclic N,N-dialkoxyamines [1, 7], in reactions of N-chloro-N-alkoxyamines [10, 21], N-alkoxy-N-arenesulfonyloxyamines [23], and N-chloro-N-alkoxyamides [24]. Dialkoxynitrenium ions were assumed to be intermediates in the transformations of N-chloro-N,N-dialkoxyamines [25]. The participation of nitrenium ions in the reactions of amines $R_2N–X$, where X is a nucleofuge or a group which readily transforms into a leaving group in the course of the reaction, is widely discussed in [26]. However, the difference between the formation of discrete nitrenium ions and particles in which the N atom has a partial positive charge is not always considered. Indisputable evidence for the existence of nitrenium ions was obtained only in the case of diarylnitrenium ions [27, 28] and the –S–N^+–S– ions, isolated in the form of salts with a weakly nucleophilic anion – AsF_6^- [29, 30].

The transformation of the bicyclic compound **H** [31] is possibly also explained by a rearrangement scheme of compound **D**.



H R=C_6H_5, CH_3O_2C

In this case, the $n\pi_{(O)}$–$\sigma^*_{N-O_{(2)}}$ electron transfer is possibly preferential over the donor–acceptor interaction (the bonding orbital of the C–CH_3 bond – the antibonding orbital of the N–$O_{(2)}$ bond), responsible for the synchronous shift of the CH_3 group, which is also the reason for the heterolysis of the N–$O_{(2)}$ bond. In fact, the bonding orbital of the C–C bond is a weak nucleophile, as confirmed by the following series of the migrating ability of groups: Ph > RO_2C > CH_3 [32].

EXPERIMENTAL

The PMR spectra were obtained on Bruker-80SY and Bruker WM-400 spectrometer, using TMS as internal standard.

The mass spectra were recorded on a Kratos MS-80-RF mass spectrometer with the energy of the ionizing electrons of 70 eV. The optical density was measured on a Polamat-A polarimeter. Isoxazolidine I was obtained by the method described in [33], bp 96-97°C (2 gPa). Isoxazolidine (s)-(+)-I was obtained according to [12], $[\alpha]_{546}$ 18°C (c 2.0 MeOH), optical purity ~3%. The optical purity and absolute configuration were determined according to [12, 13].

Reaction of Isoxazolidine I with $SbCl_5$. A solution of 0.21 g (1 mmole) of isoxazolidine I in 3 ml of CCl_4 was added at –40°C to a solution of 0.59 g (2 mmoles) of $SbCl_5$ in 4 ml of ethyl chloride. The solvent was decanted, the residue was washed with CCl_4 and dried in vacuo. PMR spectrum (80 MHz, CD_2Cl_2): 3.53 (2H, t, ^3J = 11, CH_2); 4.0 (3H, s, CH_3O); 4.88 ppm (2H, t, CH_2O). The product was treated with a solution of 0.2 g (2 mmoles) of triethylamine in 5 ml of methanol. The mixture was evaporated and the residue was extracted with ether. The extract was evaporated, and the residue was chromatographed on a column (SiO_2 L 40/100, ether). Yield 0.1 g (77%) of methyl isoxazoline-3-carboxylate (III). The product was identified by comparison with an authentic sample according to the PMR spectrum [34].

Reaction of Isoxazolidine I with $SbCl_5$ and Methanol. A solution of 0.33 g (1.5 mmoles) of isoxazolidine I in 5 ml of CCl_4 was added dropwise at –40°C, with stirring, to a solution of 0.89 g (3 mmoles) of $SbCl_5$ in 10 ml of ethyl chloride. A gel-like precipitate separated out. The mixture was treated at –78°C with a solution of 0.76 g (7.5 mmoles) of triethylamine in 10 ml of absolute methanol, and then was evaporated. The residue was extracted with ether, the extract was evaporated, and the residue was chromatographed on a column (SiO_2, L 40/100, ether). Yield 0.02 g (10%) of isoxazoline III and 0.16 g (49%) of isoxazolidine II, identified by comparison with an authentic sample according to the PMR spectrum [2].

Reaction of Isoxazolidine I with $SbCl_5$ and Ethanol. According to the preceding method, from 2.89 g (9.6 mmoles) of $SbCl_5$, 1.06 g (4.8 mmoles) of isoxazolidine I, 2.44 g (24.2 mmoles) of triethylamine and 10 ml of absolute ethanol, after chromatography on a column, 0.07 g (7%) of isoxazolidine II and 0.28 g (25%) of methyl 2-carbomethoxy-3-ethoxyisoxazolidine-3-carboxylate IV, $C_9H_{15}NO_6$, mp 56-57°C (from ether at 0°C) were obtained. PMR spectrum (400 MHz, $CDCl_3$): 1.24 (3H, t, ^3J = 7.1 Hz, CH_3 in CH_3CH_2); 2.60 and 2.70 (2H, m, ^2J = –12.7; ^3J 6.1; ^3J = 6.8 Hz, CCH_2C); 3.68 and 3.96 (2H, m, ^2J = –9.5 Hz, CH_2 in CH_3CH_2); 3.80 (3H, s, CH_3O); 3.81 (3H, s, CH_3O); 4.19 and 4.25 ppm (2H, m, ^2J = –7.7 Hz, CH_2O); m/z (I_{rel}, %): 233 $[M]^{+\cdot}$ (6), 174 $[M–CH_3O_2C]^+$ (100), 146 $[M–CH_3O_2C–C_2H_4]^+$ (81), 102 (74). Found: M 233.

Reaction of Isoxazolidine (s)-(+)-I with ETB. A mixture of 0.28 g (2 mmoles) of ETB and 5 ml of CCl_4 was added dropwise at 0°C, with stirring, to a solution of 0.44 g (2 mmoles) of isoxazolidine (s)-(+)-I in 5 ml of CCl_4. After 2 h, the reaction mixture was neutralized with an aqueous solution of $NaHCO_3$, the organic phase was separated, dried over $MgSO_4$, evaporated under vacuum, and the residue was crystallized from ether at 0°C. Yield 0.32 g (73%) of isoxazolidine (+)-II, mp 71°C, $[\alpha]_{546}$ 0.4°, $[\alpha]_{436}$ 1.1° (c 2.7 MeOH). The product was identified by comparison with an authentic racemic sample according to the PMR spectrum [2]. The optical purity of the product (~3%) was determined by the PMR method (400 MHz, $CDCl_3$), using the chiral shift-reagent $Eu(tfc)_3$. The maximal separation of the signals (CH_3O_2C) of the enantiomers is obtained at $C_{P/S}$ = 0.47.

Dimethyl 2-(2-Chloro-2-methylpropyl)isoxazolidine-3,3-dicarboxylate (V, $C_{11}H_{18}NO_5Cl$). A solution of 2.99 (10 mmoles) of $SbCl_5$ in 5 ml of CH_2Cl_2 was added dropwise at –78°C, with stirring, to a solution of 1.1 g (5 mmoles) of isoxazolidine I and 15 ml of isobutylene in 10 ml of CH_2Cl_2. The temperature was raised to room temperature, and the mixture was neutralized with a solution of 3.03 g (30 mmoles) of triethylamine in 10 ml of CH_2Cl_2, and was then diluted with ether. The precipitate was separated, the filtrate evaporated, and the residue was extracted with ether. The extract was evaporated and the product was chromatographed on a column (SiO_2 L 40/100, ether–hexane, 1:1). Yield 1.1 g (78%) of

isoxazolidine V. PMR spectrum (400 MHz, $CDCl_3$): 1.62 (6H, s, CH_3C), 2.76 (2H, t, ^3J = 7.3 Hz, CCH_2C), 3.28 (2H, s, CH_2N), 3.79 (6H, s, CH_3O_2C), 3.91 ppm (2H, t, CH_2O). m/z (I_{rel}, %): 281 $[M + 2]^{+\cdot}$ (2), 279 $[M]^{+\cdot}$(6), 244 $[M - Cl]^+$ (9), 220 $[M - CH_3O_2C]^+$ (20), $[M - C_3H_6Cl]^+$ (100). Found: M 279.

Dimethyl 2-(1-Methoxyethyl)isoxazolidine-3,3-dicarboxylate (VII, $C_{10}H_{17}NO_6$). A solution of 1.4 g (10 mmoles) of ETB in 5 ml of ether was added at 0°C to a solution of 1.1 g (5 mmoles) of isoxazolidine in 5 ml of ether and the mixture was allowed to stand overnight at –4°C. The solvent was decanted, the residue was washed with ether and dried in vacuo. Yield 1.2 g (69%) of isoxazolidine VI. PMR spectrum (80 MHz, $CDCl_3$): 1.25 (3H, t, ^3J = 7.0 Hz, CH_3 in CH_3CH_2); 2.68 (3H, d, ^3J = 6.0 Hz, CH_3CH);' 3.35 (2H, t, ^3J = 7.0 Hz, CCH_2C), 3.70 (2H, q, CH_2 in CH_3CH_2); 3.97 (6H, s, CH_3O); 4.75 (2H, t, CH_2O); 8.58 ppm (1H, q, CH). A solution of 1.01 g (10 mmoles) of triethylamine in 10 ml of methanol was added to the product, the solvent was evaporated under vacuum, the residue was extracted with ether, and the extract was evaporated. Yield 0.84 g (68%, based on isoxazolidine I) of product VI, which was pure according to PMR and which decomposed on distillation in vacuum and chromatography on SiO_2, and partially decomposed on Al_2O_3. The product was purified by column chromatography (Al_2O_3-neutral ether). PMR spectrum (400 MHz, C_6D_6): 1.46 (3H, d, CH_3 in CH_3CH); 2.75 and 2.80 (2H, m, ^2J = –12.2 Hz, CCH_2C); 3.09 (3H, s, CH_3O); 3.31 and 3.33 (6H, d, CH_3O_2C); 3.69 (1H, m, ^2J = –9.0; ^3J = 6.4; ^3J = 8.5 Hz, CH_2CHO); 3.81 (1H, m, ^2J = –9.0; ^3J = 6.6; ^3J = 6.8 Hz, CH_2CHO); 4.92 ppm (1H, q, CH). Found: M 247.

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REARRANGEMENTS OF 1-OXA-2-AZOLES.

2.* STRUCTURE AND ISOMERIZATION OF PENTAMETHYLENE-AMIDOXIMES OF 4-AMINOFURAZAN-3-CARBOXYLIC ACID

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UDC 547.793.2

The Z-oxime of the pentamethyleneamide of 4-aminofurazan-3-carboxylic acid isomerizes – rapidly in acid media, slowly in the absence of acid – to the E-oxime which at 120-140°C undergoes alkali-catalyzed rearrangement to 4-piperidinofurazan-3-carboxyamidoxime.

The amidoxime of 4-aminofurazan-3-carboxylic acid (I), at 120-140°C in the presence of alkali, undergoes a degenerative rearrangement [1]:

Ia Ib

*For Communication 1 see [1].

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