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Unusual formation of imidazooxazolone in the reaction of 1-[(2-acetylamino)ethyl]imidazolone with KSCN in the presence of AcOH

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Dedicated to Professor Oleg A. Rakitin on the occasion of his 65th anniversary

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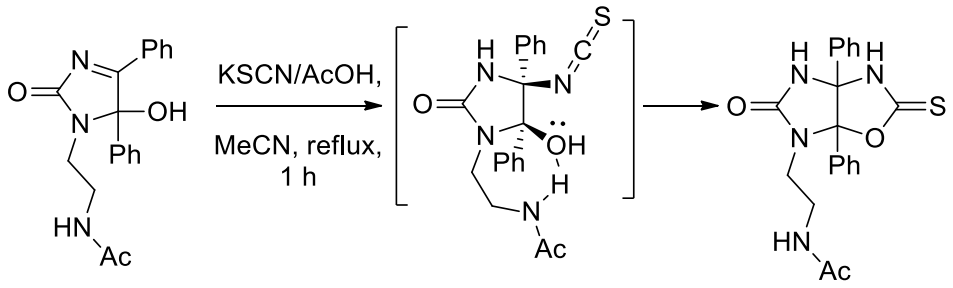
Abstract

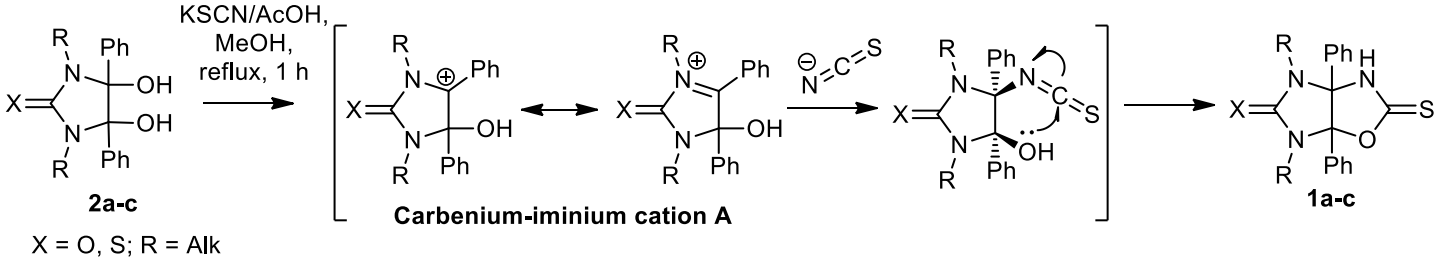
1-[(2-Acetylamino)ethyl]imidazolone was introduced for the first time in the condensation with KSCN in the presence of AcOH and imidazooxazolone was unexpectedly obtained. This result was possible only because of the unique character of 1-((2-acetylamino)ethyl)imidazolone, which has an intramolecular N-H···O-H hydrogen bond and, therefore, reacts with the NCS anion to give only imidazooxazolone.



Keywords: Glycoluril analogues, fused oxazolinones, imidazolinones, KSCN, AcOH, X-ray diffraction

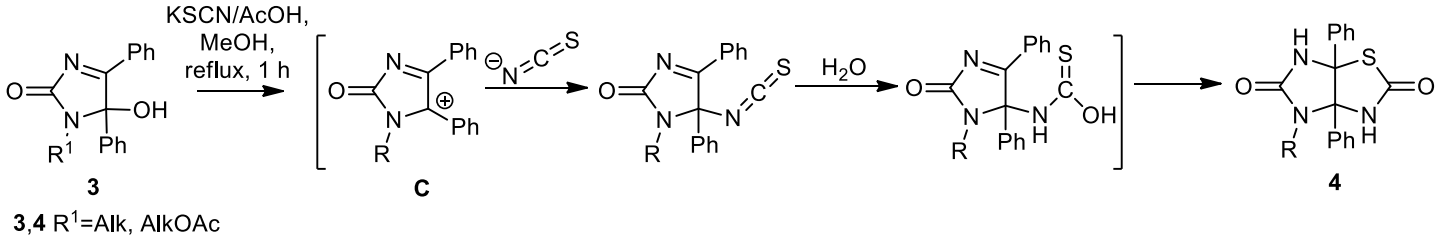
Introduction

It is known that imidazole and oxazole moieties are present in the molecules of pharmaceutical compounds (e.g., the most well-known biotin, and mebicar drugs[1]) and biologically active compounds.[1-12] Compounds containing these moieties in the same molecule are difficult to prepare.[13-16] Our many-year experience in the synthesis and investigations of tetrahydroimidazo[4,5-*d*]imidazole-2,5(1*H*,3*H*)-diones (glycolurils) and their hetero analogs[6-8,17-29] allowed us to propose a new method for the synthesis of 4,6-dialkyl-3a,6a-diphenyltetrahydro-2*H*-imidazo[4,5-*d*]oxazole-2,5(3*H*)-dithiones and 4,6-dimethyl-3*a*,6*a*-diphenyl-2-thioxo-tetrahydro-2*H*-imidazo[4,5-*d*]oxazol-5(3*H*)-one (imidazooxazolones) **1a-c** based on the reaction of 4,5-dihydroxy-4,5-diphenylimidazole-2-ones(thiones) **2a-c** with KSCN in the presence of AcOH (Scheme 1).[28]



Scheme 1. Synthesis of imidazooxazolones **1a-c** and mechanism of their formation

Considering the proposed mechanism, the formation of imidazooxazolone proceeds via carbenium-iminium cation **A**, which is an analogue of the 1-substituted 5-hydroxy-4,5-diphenyl-1*H*-imidazole-2(5*H*)-ones (imidazolones) **3**. Therefore, the condensations of imidazolones **3** with KSCN in AcOH were studied, and 4-substituted 3*a*,6*a*-diphenyl-2-thioxotetrahydro-2*H*-imidazo[4,5-*d*]thiazol-5(3*H*)-ones (imidazothiazolones) **4** were unexpectedly formed (Scheme 2).[29] We interpreted the obtained result in terms of a different mechanism (via the formation of carbocation **C**).



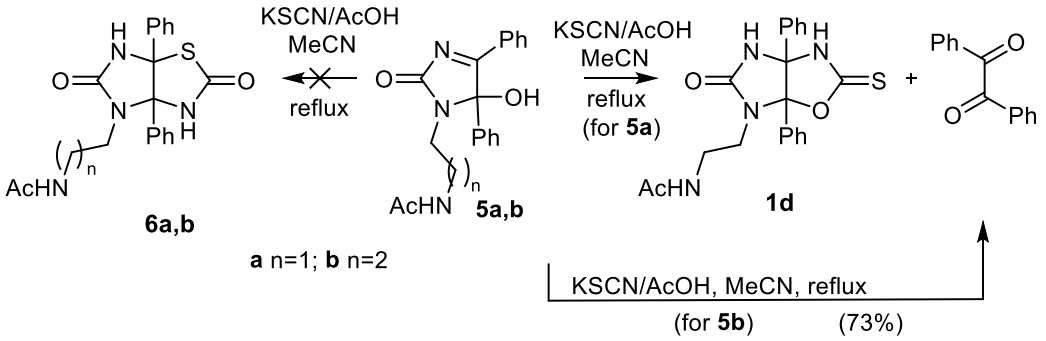
Scheme 2. Synthesis of imidazothiazolones **4** and mechanism of their formation

Results and Discussion

To extend the scope of applicability of KSCN, in this study, *N*-[(5-hydroxy-2-oxo-4,5-diphenyl-2,5-dihydro-1*H*-imidazol-1-yl)alkyl]acetamides (further 1-[(acetylamino)alkyl]imidazolones) **5a**,**b** were introduced for the first time in the condensation with KSCN in the presence of AcOH (Table 1, entry 1: MeCN, reflux, 1 h, 12 mol eq. AcOH). The reactions were carried out under conditions of obtaining imidazothiazolones **4**.[29] This reaction led to an unusual outcome, namely, imidazooxazolone **1d** was formed instead of the expected imidazothiazolone **6a** (Table 1). Imidazooxazolone **1d** precipitated from the reaction mixture as crystals (yield 27%). No other heterocyclic products were isolated from the filtrate upon evaporation to a resin-like residue, but has been allocated a well-known 1,2-dioxo-1,2-diphenylethane (benzil). It is a product of the competing process of

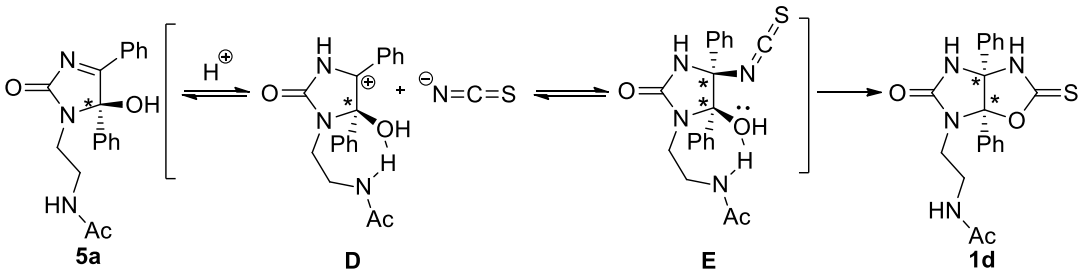
hydrolysis of the source imidazolone **5a**. Change of the reaction times, the temperature of the reaction mixture and the amount of AcOH did not lead to any increase in the yield of compound **1d** (Table 1, entries 2-7). Imidazolone **5b** does not interact with KSCN in the presence of AcOH and is hydrolyzed to benzil (Table 1, entry 8).

Table 1. The reaction of 1-[(acetylamino)alkyl]imidazolones **5a**,**b** with KSCN in the presence of AcOH



Entry	reagent	Time, h	T, °C	AcOH, mol eq.	Yield, (%)
1	**5a**	1	reflux	12	**1d** (27), benzil (57)
2	**5a**	1.5	reflux	12	**1d** (27), benzil (68)
3	**5a**	0.5	reflux	12	**1d** (10), benzil (24)
4	**5a**	1	reflux	6	**1d** (7), benzil (10)
5	**5a**	1	reflux	18	**1d** (13), benzil (76)
6	**5a**	1	50	12	**1d** (6), benzil (48)
7	**5a**	1	r.t.	12	-
8	**5b**	1	reflux	12	benzil (73)

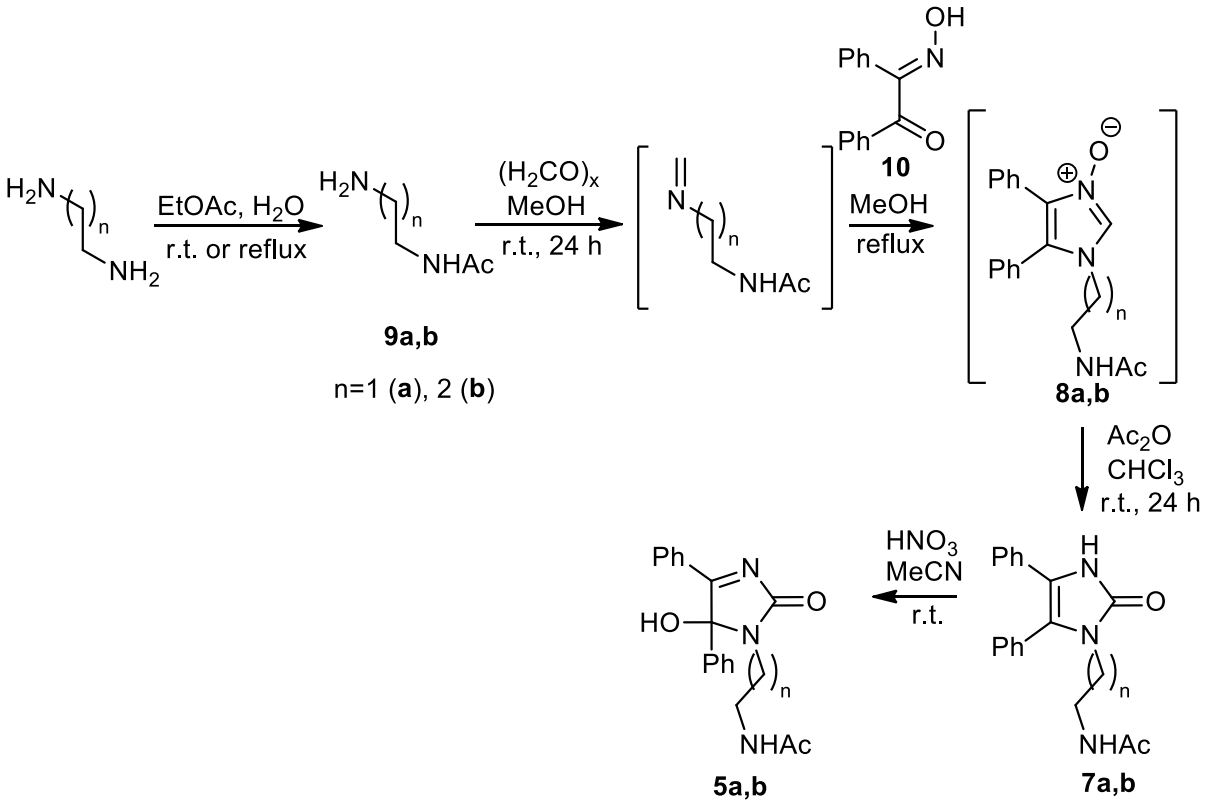
This unusual result can be attributed to the presence of the NH group in the substituent of starting compound **5a**. Apparently, owing to the formation of the intramolecular N-H…O-H hydrogen bond the C(4)=N(3) bond is protonated giving cation **D**, which adds the isothiocyanate anion. The intramolecular cyclization of the intermediate **E** thus formed yields product **1d** (Scheme 3).



Scheme 3. Plausible mechanism for the formation of imidazooxazole **1d**

Procedures were developed for the synthesis of previously unknown starting imidazolones **5a**,**b** based on the reactions of 1-(acetylaminoalkyl)imidazolinones **7a**,**b** with concentrated nitric acid in MeCN. Compounds **7a**,**b** were prepared by Ac_2O-induced rearrangenment of *N*-oxides **8a**,**b**. This approach was chosen considering published data on the synthesis of 1-substituted imidazolinones.[29-34] *N*-Oxides **8a**,**b** were synthesized by

condensation of accessible reactants: N-acetylalkylenediamines **9a**,**b** (prepared by acylation of ethylenediamine[35-37] or prophylendiamine[38]), paraformaldehyde, and α-ketooxime **10** (Scheme 4).



Scheme 4. Synthesis of imidazolones **5a,b**

The structures of the obtained compounds **1d**, **5a**,**b** and **7a**,**b** were proved by a set of methods including ^{1}H and ^{13}C NMR spectroscopy and high-resolution mass spectrometry.

The structures of **1d** and **7a** have been additionally confirmed by X-ray diffraction (Figures 1A, 2A). According to the X-ray diffraction data, the compound **1d** crystallizes in a centrosymmetric space group P $2_1/n$ with two symmetry-independent molecules; those are held together by N(1)-H…O(1) hydrogen bonds (N…O 2.877(2) and 2.884(2) Å, NHO 165(1) and 166(1)°) resulting in a pseudo-centrosymmetric dimer (Figure 1B). The two molecules have similar geometry, and the only difference is the positioning of the aliphatic substituent at the N(2) atom relative to the N(2)-C(2) bond: transoid in one molecule, cisoid in the other. Molecules of the first type form infinite H-bonded chains via the C=O group of the Ac functionality (N…O 2.718(2) Å, NHO 164(1)°), which in the case of the molecules of the second type leads to centrosymmetric dimers (N…O 2.776(2) Å, NHO 177(1)°). Together, they result in H-bonded columns, which are additionally stabilized by a short S…O contact (S…O 3.230(1) Å) that occurs between the molecules of the different types.
The compound **7a** also crystallizes in the space group P $2_1/n$ but with one symmetry-independent molecule, which forms centrosymmetric dimers by N(1)-H…O(1) hydrogen bonds (N…O 2.755(4) Å, NHO 176(4)°) and infinite H-bonded chains via the C=O group of the amide fragment (N…O 2.961(4) Å, NHO 169(5)°) (Figure 2B). In both cases, the 3D framework is completed through numerous weaker interactions, which include C-H…O, N-H…π (in **1d**), C-H…π, H…H, etc.

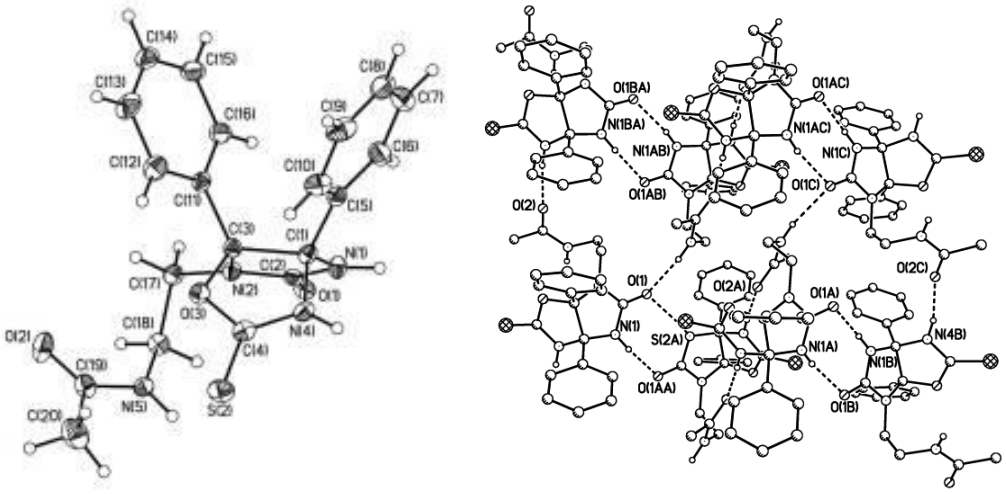


Figure 1: A. General view of one independent molecule **1d** with atoms shown as thermal ellipsoids (p=50%). **B.** A fragment of the H-bonded column featuring the centrosymmetric dimers in the center and infinite chains on each side.

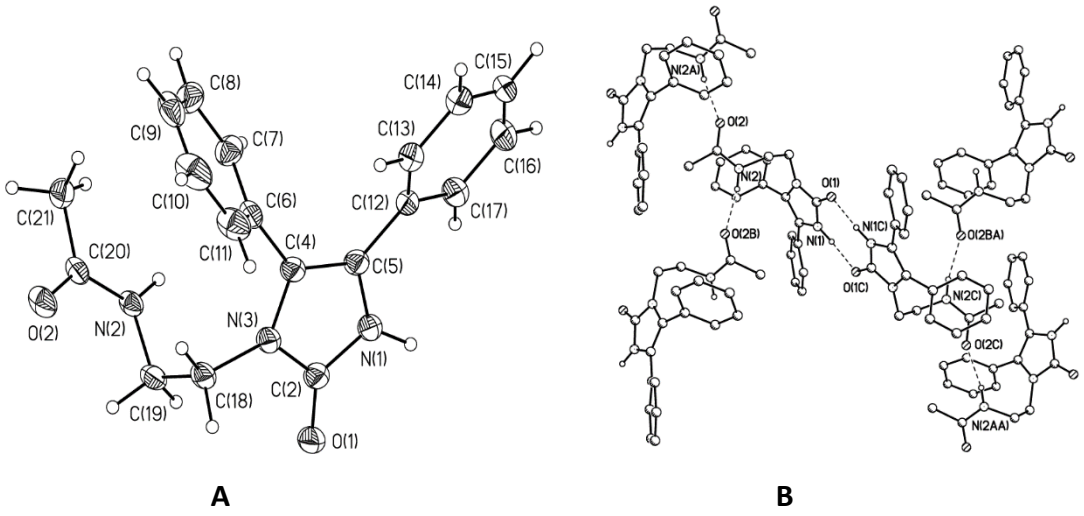


Figure 2: A. General view of the molecule **7a** with atoms shown as thermal ellipsoids (p=50%). **B.** A fragment of the crystal packing featuring the centrosymmetric dimer in the center and infinite chains on each side

Conclusions

Thus, the condensations of 1-((2-acetylamino)alkyl)imidazolones **5a,b** with KSCN in the presence of AcOH, studied for the first time, led to an unusual result, namely, afforded imidazooxazolone **1d** instead of the expected imidazothiazole **6a**. This was possible only because of the unique character of imidazolone **5a**, which has an intramolecular N-H···O-H hydrogen bond and, therefore, reacts with the NCS anion to give only imidazooxazolone **1d**. It is shown that imidazolone **5b** hydrolyzed to benzil under analogous conditions. Procedures for the synthesis of previously unknown starting compounds, imidazolone **5a**,**b** and imidazoline **7a**,**b**, were developed.

Experimental Section

General. All reagents were purchased from commercial sources and used without treatment, unless otherwise indicated. The product were purified by recrystallization. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-300 spectrometer (300,13 and 75,13 MHz, respectively) in DMSO-d_6 with TMS as internal standard. MS and ESI were recorded using Kratos MS-30 and Bruker MicrOTOF II mass spectrometers respectively. Elemental analyses were performed on a Perkin Elmer 2400 Elemental CHN analyzer and Euro EA elemental Analyzer.

***N*-[2-(5-Oxo-3a,6a-diphenyl-2-thioxotetrahydro-2*H*-imidazo[4,5-*d*]oxazol-6(6a*H*)-yl)ethyl]acetamide** (**1d**). AcOH (3.00 ml) was added to a solution of the imidazolone **5a** (1.35 g, 4 mmol) and KSCN (0.44 g, 4.5 mmol) in MeCN (17 ml) at r.t., and the mixture was refluxed for 1h. The mixture was allowed to cool to r.t. and kept for 24 h to give a precipitate **1d**. Colorless crystals (0.68 g, 27%), mp 250-252 °C. ^{1}H-NMR (300 MHz, DMSO-d_6): δ 1.74 (s, 3 H, Ac), 2.76 – 2.90 (m, 1 H, CH_2), 3.08 – 3.29 (m, 2 H, CH_2), 3.30 – 3.44 (m, 1 H, CH_2), 6.89 – 7.10 (m, 4 H, Ph), 7.11 – 7.22 (m, 6 H, Ph), 7.82 (t, 1 H, *J* 5.1 Hz, NH), 9.02 (s, 1 H, NH), 11.52 (s, 1 H, NH). ^{13}C-NMR (75 MHz, DMSO-d_6): δ 22.58 (Me), 37.40, 40.47 (CH_2), 83.51 (C-O), 106.66 (C-N) 126.82, 126.87, 127.92, 128.25, 128.95, 129.34, 132.12, 134.58 (Ph), 157.98, 169.18 (C=O), 187.16 (C=S). HRMS (EI): *m/z* calcd for $C_{20}H_{20}N_4O_3S+H^+$: 397.1329; found: 397.1321.

General procedure for the synthesis of *N*-[2-(5-hydroxy-2-oxo-4,5-diphenyl-2,5-dihydro-1*H*-imidazol-1-yl)-ethyl]acetamide (5a) and *N*-[3-(5-hydroxy-2-oxo-4,5-diphenyl-2,5-dihydro-1*H*-imidazol-1-yl)propyl]acet-amide (5b). 63% aq. HNO_3 (5ml) was added dropwise to a suspension of the appropriate imidazolinone **7a,b** (4 mmol) in MeCN (25 ml). The reaction was monitored by the dissolution of the precipitated **7** and by the change in color of the solution. The mixture was then extracted with 1:1 $CHCl_3/H_2O$, the $CHCl_3$ layer was evaporated (for **5b**), and the product **5a** was crystallized from $CHCl_3$.

***N*-[2-(5-Hydroxy-2-oxo-4,5-diphenyl-2,5-dihydro-1*H*-imidazol-1-yl)ethyl]acetamide** (**5a**). White solid (0.86 g, 64%), mp 275-276 °C. ^{1}H-NMR (300 MHz, DMSO-d_6): δ 1.72 (s, 3 H, Ac), 2.82 (dt, 1 H, ^{2}J 13.7 Hz, ^{3}J 6.7 Hz, CH_2), 3.00 – 3.13 (m, 2 H, CH_2), 3.27 (dt, 1 H, ^{2}J 13.7 Hz, ^{3}J 7.2 Hz, CH_2), 7.30 – 7.48 (m, 7 H, Ph), 7.53 – 7.58 (m, 1 H, Ph), 7.74 (t, 1 H, ^{3}J 5.6 Hz, NH), 7.82 (s, 1 H, OH), 7.07 – 8.05 (m, 2 H, Ph). ^{13}C-NMR (75 MHz, DMSO-d_6): δ 22.51 (Me), 38.22, 38.47 (CH_2), 92.88 (C-OH), 125.21, 128.57, 128.76, 128.90, 129.01, 129.66, 133.45, 136.80 (Ph), 163.81, 169.50 (C=O), 186.34 (C=N). MS: *m/z* (%) 337 (40), 323 (2), 305 (3), 278 (90), 265 (16), 253 (12), 237 (11), 209 (54), 194 (65), 180 (68), 166 (28), 131 (6), 104 (45), 85 (100). Anal. calcd for $C_{19}H_{19}N_3O_3$: C: 67.64; H: 5.68; N: 12.46; found: C: 67.67; H: 5.66; N: 12.42.

***N*-[3-(5-Hydroxy-2-oxo-4,5-diphenyl-2,5-dihydro-1*H*-imidazol-1-yl)propyl]acetamide (5b)**. Yellowish solid (1.00 g, 71%), mp 85-87 °C. ^{1}H-NMR (300 MHz, DMSO-d_6): δ 1.30 – 1.46 (m, 1 H, CH_2), 1.47 – 1.60 (m, 1 H, CH_2), 1.76 (s, 3 H, Ac), 2.76 – 2.87 (m, 1 H, CH_2), 2.88 – 2.98 (m, 2 H, CH_2), 3.14 – 3.26 (m, 1 H, CH_2), 7.33 – 7.48 (m, 7 H, Ph), 7.51 – 7.58 (m, 1 H, Ph), 7.75 – 7.85 (m, 2 H, NH+OH), 7.82 (1H, s, OH), 7.98 - 8.04 (m, 2 H, Ph). ^{13}C-NMR (75 MHz, DMSO-d_6): δ 22.59 (Me), 28.54, 36.47, 37.10 (CH_2), 92.99 (C-OH), 125.20, 128.73, 128.83, 128.96, 129.09, 129.73, 133.47, 137.13 (Ph), 163.78, 169.17 (C=O), 186.26 (C=N). HRMS (EI): *m/z* calcd for $C_{20}H_{21}N_3O_3+H^+$: 352.1656; found: 352.1649.

General procedure for the synthesis of *N*-[2-(2-oxo-4,5-diphenyl-2,3-dihydro-1H-imidazol-1-yl)ethyl]-acetamide (**7a**) **and *N*-[3-(2-oxo-4,5-diphenyl-2,3-dihydro-1H-imidazol-1-yl)propyl]acetamide** (**7b**): To a mixture of corresponding *N*-(aminoalkyl)acetamide (**9a,b**) (30 mmol) and paraformaldehyde (1.28 g, 40 mmol), MeOH (50 mL) was added. The reaction mixture was stirred at room temperature for 24 h and was then evaporated to dryness. The obtained mixture was dissolved in MeOH (50 mL), and 2-(hydroxyimino)-1,2-diphenylethanone (**10**) (6.36 g, 30 mmol) was added. The reaction mixture was refluxed for 3 h. After that, it was evaporated to dryness. The obtained mixture was added $CHCl_3$ (20 mL), a solution of Ac_2O (6.4 mL, 62.5 mmol) in $CHCl_3$ (10 mL) was added dropwise over 30 min with cooling on an ice bath. The reaction mixture

was stirred at room temperature for 24 h, after which EtOH (30 mL) was added. The mixture was stirred for 30 min, evaporated to dryness. After addition of EtOH (20 mL) the mixture was allowed to crystallize. The crystals of the product **7** were filtered off and washed with EtOH.

***N*-[2-(2-Oxo-4,5-diphenyl-2,3-dihydro-1*H*-imidazol-1-yl)ethyl]acetamide** (**7a**). Colorless crystals (2.31 g, 18%), mp 275-276 °C. ^{1}H-NMR (300 MHz, DMSO-d_6): δ 1.67 (s, 3 H, Ac), 3.04 – 3.12 (m, 2 H, CH_2), 3.45 (t, 2 H, *J* 6.1 Hz, CH_2), 7.09 – 7.22 (m, 5 H, Ph), 7.33 – 7.40 (m, 2 H, Ph), 7.43 – 7.50 (m, 3 H, Ph), 7.87 (t, 1 H, *J* 5.7 Hz, NH), 10.79 (s, 1 H, NH). ^{13}C-NMR (75 MHz, DMSO-d_6): δ 22.48 (Me), 37.64, 40.18 (CH_2), 117.10, 120.68, 125.23, 126.35, 128.30, 128.87, 129.02, 129.60, 129.75, 130.90 (Ph-C=C-Ph), 153.23, 169.07 (C=O). MS: *m/z* (%) 321 (10), 292 (2), 262 (3), 250 (4), 245 (1), 224 (5), 209 (4), 193 (5), 178 (5), 170 (4), 161 (5), 135 (100). Anal. calcd for $C_{19}H_{19}N_3O_2$: C: 71.01; H: 5.96; N: 13.08; found: C: 71.04; H: 5.99; N: 13.04.

***N*-[3-(2-Oxo-4,5-diphenyl-2,3-dihydro-1*H*-imidazol-1-yl)propyl]acetamide** (**7b**). White solid (2.95 g, 22%), mp 248-250 °C. ^{1}H-NMR (300 MHz, DMSO-d_6): δ 1.41 – 1.53 (m, 2 H, CH_2), 2.83 – 2.95 (m, 2 H, CH_2), 3.43 (t, 2 H, *J* 6.7 Hz, CH_2), 7.09 – 7.23 (m, 5 H, Ph), 7.33 – 7.42 (m, 2 H, Ph), 7.43 – 7.53 (m, 3 H, Ph), 7.67 – 7.74 (m, 1 H, NH), 10.81 (s, 1 H, NH). ^{13}C-NMR (75 MHz, DMSO-d_6): δ 22.56 (Me), 29.18, 35.90, 38.34 (CH_2), 117.24, 120.38, 125.32, 126.44, 128.34, 128.91, 129.11, 129.66, 130.72 (Ph-C=C-Ph), 153.09, 168.83 (C=O). HRMS (EI): *m/z* calcd for $C_{20}H_{21}N_3O_2$+H^+: 336.1707; found: 336.1702.

X-Ray Structural Analysis. X-ray diffraction data for **1d** and **7a** were collected on Bruker APEX2 DUO CCD difractometer (λ(MoKα) = 0.71072Å, ω-scans). Frames were integrated using the Bruker SAINT software package[39] by a narrow-frame algorithm. A semiempirical absorption correction was applied with the SADABS[40] program using the intensity data of equivalent reflections. The structure of **7a** was a non-mirohedral twin. The intensities of overlapping reflections were corrected with algorithms implemented in PLATON software package[41]. The structures were solved with direct methods and refined by the full-matrix least-squares technique against F^2_{hkl} in anisotropic approximation for non-hydrogen atoms with SHELX[42] software package. The hydrogen atoms of NH groups were found from difference Fourier synthesis and refined isotropically. The positions of other hydrogen atoms were calculated, and all hydrogen atoms were refined in riding model with $U_{iso}(H) = 1.5U_{eq}(C_m)$ and $1.2U_{eq}(C_i)$, where $U_{eq}(C_m)$ and $U_{eq}(C_i)$ are respectively the equivalent thermal parameters of the methyl carbon and all other carbon atoms to which corresponding H atoms are bonded. Crystallographic and refinement data for **1d** ($C_{20}H_{20}N_4O_3S$, M = 396.46): at 100 K crystal is monoclinic, space group P 2_1/n, a = 8.5594(6), b = 16.7142(11), c = 26.7139(17) Å, β = 93.9180(10)°, V = 3812.9(4) Å^3, Z = 8 (Z' = 2), d_{calc} = 1.381 gcm^{-3}, μ(MoKα) = 1.99 cm^{-1}, F(000) = 1664; refinement converged to R1 = 0.0537 (calculated for 6812 observed reflections with I>2σ(I)), wR2 = 0.1615 and GOF = 1.082 (for 9210 independent reflections, 2θ<56°). For **7a** ($C_{19}H_{19}N_3O_2$, M = 321.37): at 100 K crystal is monoclinic, space group P 21/n, at 100K: a = 12.174(3), b =9.774(3), c = 14.459(4) Å, β = 105.453(5)°, V = 1658.2(8) Å^3, Z = 4 (Z' = 1), d_{calc} = 1.287 gcm^{-3}, μ (MoKα) = 0.85 cm^{-1}, F(000) = 680; refinement converged to R1 = 0.0737 (calculated for 2751 observed reflections with I>2s(I)), wR2 = 0.2380 and GOF = 1.083 (for 3605 independent reflections, 2θ<54°); refined BASF parameter for twin components were 0.168. CCDC 1453338 and 1530568 contain supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Supplementary Material

^{1}H, ^{13}C NMR spectra of compounds **1d**, **5a**,**b** and **7a**,**b**.

References

1. Mashkovskii, M. D. *Lekarstvennye Sredstva [Drugs]*; Novaya Volna: Moscow, 2014.
2. Greenlee, W. J.; Johnston, D. B. R.; MacCoss, M.; Mantlo, N. B.; Patchett, A. A.; Chakravarty, P. K.; Walsh, T. F. EP Patent 407102 (Chem. Abstr. **1993**, *115*, 49693k).
3. Alban, C. *Advances in Botanical Research*, eds. F. Rebeille and R. Douce; Elsevier: Amsterdam; 2011, Vol. 59, pp 40-43.
4. Fernandez-Mejia, C.; Lazo-de-la-Vega-Monroy, M. -L. *Evidence-based Compl. and Alt. Medicine* **2011**, *16*, 40. http://dx.doi.org/10.1177/1533210110392947
5. Kamburg, R. US Patent 227838 (Chem. Abstr. **2008**, *149*, 347537).
6. Ryzhkina, I. S.; Kiseleva, Y. V.; Mishina, O. A.; Timosheva, A. P.; Sergeeva, S. Y.; Kravchenko, A. N.; Konovalov, A. I. *Mendeleev Commun.* **2013**, *23*, 262. http://dx.doi.org/10.1016/j.mencom.2013.09.008
7. Ryzhkina, I. S.; Kiseleva, Y. V.; Murtazina, L. I.; Mishina, O. A.; Timosheva, A. P.; Sergeeva, S. Yu.; Baranov, V. V.; Kravchenko, A. N. Konovalov, A. I. *Mendeleev Commun.* **2015**, *25*, 72. http://dx.doi.org/10.1016/j.mencom.2015.01.027
8. Kravchenko, A. N.; Baranov, V. V.; Anikina, L. V.; Vikharev, Yu. B.; Bushmarinov, I. S.; Nelyubina, Yu. V. *Rus. J. Bioorg. Chem.* **2012**, *38*, 550. http://dx.doi.org/10.1134/S106816201205007X
9. Zhu, B.; Marinelli, B. A.; Abbanat, D.; Foleno, B. D.; Bush, K.; Macielag, M. J. *Bioorg. Med. Chem. Lett*. **2007**, *17*, 3900. http://dx.doi.org/10.1016/j.bmcl.2007.04.104
10. Girniene, J.; Tatibouët, A.; Sackus, A.; Yang, J.; Holman, G. D.; Rollin, P. *Carbohydr. Res*. **2003**, *338*, 711. http://dx.doi.org/10.1016/S0008-6215(03)00007-7
11. Berlyand, A. S.; Prokopov, A. A. *Pharm. Chem. J*. **2014**, *48*, 347. http://dx.doi.org/10.1007/s11094-014-1108-5
12. Berlyand A. S.; Lebedev, O. V.; Prokopov, A. A. *Pharm. Chem. J*. **2013**, *47*, 176. http://dx.doi.org/10.1007/s11094-013-0920-7
13. Kakanejadifsrd, A.; Kargar, K.; Farnia, M. F.; Bahrami Ziabari, M.; Todaro, L. J. *Polish J. Chem*. **2004**, *78*, 45.
14. Tanaka, S.; Seguchi, K.; Itoh, K.; Sera, A. *J. Chem. Soc., Perkin Trans. 1* **1994**, 2335. http://dx.doi.org/10.1039/P19940002335
15. Maligres, P. E.; Waters, M. S.; Weissman, S. A.; McWilliams, J. C.; Lewis, S.; Cowen, J.; Reamer, R. A.; Volante, R. P.; Reider, P. J.; Askin, D.; *J. Heterocyclic Chem.* **2003**, *40*, 229. http://dx.doi.org/10.1002/jhet.5570400206
16. Broan, C. J.; Butler, A. R. *J. Chem. Soc., Perkin Trans. 2* **1991**, 1501. http://dx.doi.org/10.1039/P29910001501
17. Gazieva, G. A.; Izmest'ev, A. N.; Nelyubina, Yu. V.; Kolotyrkina, N. G.; Zanin I. E.; Kravchenko, A. N. *RSC Adv*. **2015**, *5*, 43990. http://dx.doi.org/10.1039/C5RA07669B
18. Gazieva, G. A.; Karpova, T. B.; Popov, L. D.; Nelyubina, Yu. V.; Kravchenko, A. N.; *J. Heterocycl. Chem*. **2015**, *52*, 1390.

http://dx.doi.org/10.1002/jhet.2244
19. Gazieva, G. A.; Kravchenko, A. N. *J. Heterocycl. Chem*. **2015**, *52*, 1858. http://dx.doi.org/10.1002/jhet.2305
20. Kravchenko, A. N.; Vasilevskii, S. V.; Gazieva, G. A.; Nelyubina, Yu. V. *Mendeleev Commun*. **2015**, *25*, 476. http://dx.doi.org/10.1016/j.mencom.2015.11.027
21. Kravchenko, A. N.; Chikunov, I. E.; Gazieva, G. A.; Makhova, N. N. *Mendeleev Commun*. **2016**, *26*, 136. http://dx.doi.org/10.1016/j.mencom.2016.03.018
22. Ivanov, E. V.; Batov, D. V.; Baranov, V. V.; Kravchenko, A. N.; *Thermochimica Acta* **2016**, *627-629*, 48. http://dx.doi.org/10.1016/j.tca.2016.01.010
23. Ivanov, E. V.; Lebedeva, E. Yu.; Abrosimov, V. K.; Baranov, V. V.; Gazieva, G. A.; Kravchenko, A. N. *Thermochimica Acta* **2015**, *89*, 270. http://dx.doi.org/10.1016/j.jct.2015.05.028
24. Kravchenko, A. N.; Chikunov, I. E.; Lyssenko, K. A.; Baranov, V. V. *Chem. Heterocycl. Compd.* **2014**, *50*, 1322. http://dx.doi.org/10.1007/s10593-014-1595-z
25. Kravchenko, A. N.; Baranov, V. V.; Gazieva, G. A.; Chikunov, I. E.; Nelyubina, Yu. V. *Rus. Chem. Bull., Int. Ed*. **2014**, *63*, 416. http://dx.doi.org/10.1007/s11172-014-0446-5
26. Baranov, V. V.; Antonova, M. M.; Nelyubina, Yu. V.; Kolotyrkina, N. G.; Kravchenko, A. N. *Synlett.* **2017**, DOI: 10.1055/s-0036-1588932 (in press). http://dx.doi.org/10.1055/s-0036-1588932
27. Baranov, V. V.; Nelyubina, Yu. V.; Kravchenko, A. N.; Kolotyrkina, N. G.; Biriukova, K. A. *Tetrahedron Lett*. **2015**, *56*, 6085. http://dx.doi.org/10.1016/j.tetlet.2015.09.071
28. Baranov, V. V.; Kravchenko, A. N.; Nelyubina, Yu. V. *Mendeleev Commun.* **2014**, *24*, 105. http://dx.doi.org/10.1016/j.mencom.2014.03.014
29. Kravchenko, A. N.; Antonova, M. M.; Baranov, V. V.; Nelyubina, Yu. V. *Synlett.* **2015**, *26*, 2521. http://dx.doi.org/10.1055/s-0035-1560657
30. Antonova, M. M.; Baranov, V. V.; Kravchenko, A. N. *Chem. Heterocycl. Compd*. **2015**, *51*, 395. http://dx.doi.org/10.1007/s10593-015-1716-3
31. Baranov, V. V.; Antonova, M. M.; Nelyubina, Yu. V.; Kolotyrkina, N. G.; Zanin, I. E.; Kravchenko, A. N. *Mendeleev Commun*. **2014**, *24*, 173. http://dx.doi.org/10.1016/j.mencom.2014.04.017
32. Antonova, M. M.; Baranov, V. V.; Nelyubina, Yu. V.; Kravchenko, A. N. *Chem. Heterocycl. Compd.* **2014**, *50*, 503. http://dx.doi.org/10.1007/s10593-014-1501-8
33. Jasiński, M.; Mlostoń, G.; Mucha, P.; Linden,A.; Heimgartner, H. *Helv. Chim. Acta* **2007**, *90*, 1765. http://dx.doi.org/10.1002/hlca.200790186
34. Mlostoń, G.; Jasiński, M.; Wróblewska, A.; Heimgartner, H. *Curr. Org. Chem*. **2016**, *20*, 1359. http://dx.doi.org/10.2174/1385272820666151210000010
35. Gazieva, G. A.; Lozhkin, P. V.; Baranov, V. V.; Kravchenko, A. N.; Makhova, N. N. *Rus. Chem. Bull., Int. Ed*. **2010**, *59*, 642. http://dx.doi.org/10.1007/s11172-010-0117-0
36. Aspinall, S. R. *J. Am. Chem. Soc.* **1941**, *63*, 852. http://dx.doi.org/10.1021/ja01848a060
37. Chegaev, K. Yu.; Kravchenko, A. N.; Lebedev, O. V.; Strelenko, Yu. A. *Mendeleev Commun.* **2001**, *11*, 32. http://dx.doi.org/10.1070/MC2001v011n01ABEH001357

38. Tang, W.; Fang, S. *Tetrahedron Lett*. **2008**, *49*, 6003. http://dx.doi.org/10.1016/j.tetlet.2008.07.174
39. Bruker, SAINT v7.23A, 2005.
40. G. M. Sheldrick, SADABS v2008/1, Bruker/Siemens Area Detector Absorption Correction Program, 2008.
41. Spek, A. L. *Acta Cryst*. **2009**, *D65*, 148-155.
42. G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr*., **2008**, *64*, 112–122.

