

Dedicated to the Full Member of the Russian Academy of Sciences
V.A. Tartakovsky on occasion of his 75th birthday

Syntheses Based on α -Azidooximes: II.* Preparation of 6,7-Dihydrotriazolopyrazinones from Aliphatic Nitro Compounds

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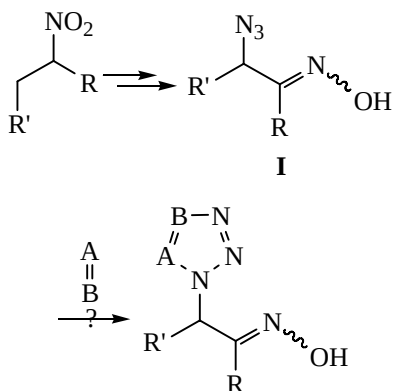
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Abstract— α -Azidooximes readily obtained from aliphatic nitro compounds were cleanly converted into previously unknown 6,7-dihydro[1,2,3]triazolo[1,5-*a*]pyrazin-4(5*H*)-ones via [3+2]-cycloaddition to dimethyl acetylenedicarboxylate and reduction of the oximino group in forming intermediates.

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We recently developed a convenient procedure for the synthesis of α -azidooximes **I** from aliphatic nitro compounds [2]. In this event α -azidooximes **I** become promising reagents for preparation of versatile polyfunctional compounds. In the previous communication [1] we reported on the opportunities involving total or partial reduction of the α -azidooximino moiety. No less promising is bringing the azido group of oximes **I** into reactions of [3+2]-cycloaddition (Scheme 1).

Scheme 1.



* For Communication I see [1].

1,3-Dipolar cycloaddition of azides is comprehensively treated in a series of monographs (see, for instance, [3]). However not a single example of the participation of azidooximes **I** in this process was described.

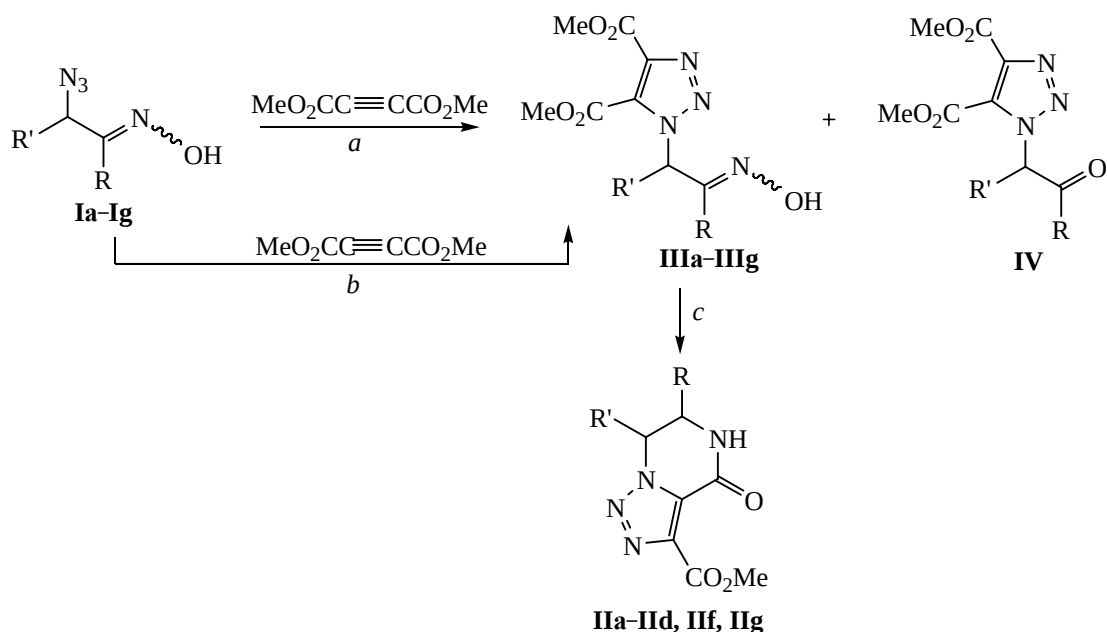
In this study the [3+2]-cycloaddition of oximes **Ia–Ig** is regarded as a key stage in the convenient preparation procedure for 6,7-dihydro[1,2,3]-triazolo[1,5-*a*]pyrazin-4(5*H*)-ones **Ila–Ilg** (Scheme 2).

Heterocycles **II** were not described in any publications. However their close analogs [1,2,3]triazolo[1,5-*a*]quinoxalin-4(5*H*)-ones **V** are well known and are found to possess a high biological activity (Scheme 3) [4–6].

Evidently the designing synthesis of heterocycles **II** and **V** is very similar. The main distinction consists in the use in the known synthesis of aromatic nitro compounds as initial substances, and the nitro group is reduced in the reduction stage; in contrast, in the newly advanced scheme nitroalkanes serve as starting reagents, and in key intermediates **III** the oximino fragment suffers reduction.

The simplest way to triazoles **III** involves the reaction of oximes **I** with dimethyl acetylenedicarboxylate **VIII** at room temperature in water containing some acetonitrile (see the table). However here the cycloaddition may be accompanied with a partial hydrolysis

Scheme 2.

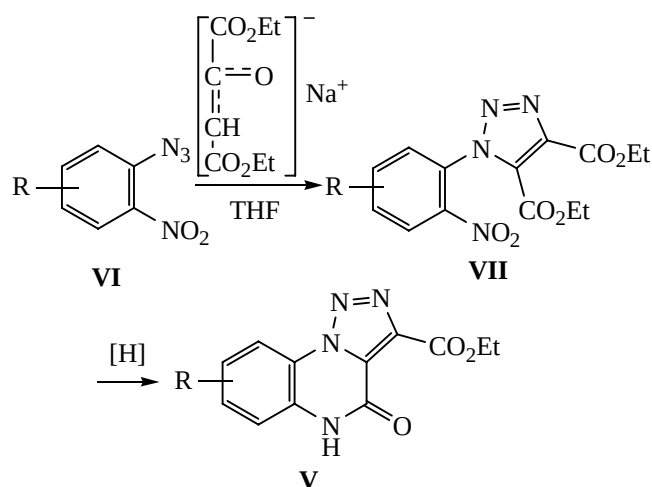


a – MeCN/H₂O, 20°C, 96 h; *b* – toluene, 20°C, 72 h; *c* – H₂ (*p* 80 at), Ni/Ra, 80°C; R = R' = H (**a**); R = H, R' = Me (**b**); R = Me, R' = H (**c**); R = Bn, R' = H (**d**); R = COOMe, R' = Me (**e**); R = CH₂OH, R' = H (**f**); R = CH₂CH₂COOMe, R' = H (**g**).

of the oximino group leading to carbonyl derivatives **IV** (see, for instance, preparation of ketone **IVc** in EXPERIMENTAL). This side process can be avoided by carrying out the [3+2]-cycloaddition **I** + **VIII** in toluene.

Oximes **III** are readily reduced on Raney nickel when R is not an ester group. In the latter case we failed to obtain target heterocycles **II**.

Scheme 3.



Compound no.	Yield, %	
	III	II (<i>c</i>) ^a
Ia	70 (<i>b</i>) ^a	85
Ib	82 (<i>a</i>) ^a	58
Ic	80 (<i>b</i>) ^a	66
Id	79 (<i>a</i>) ^a	86
Ie	78 (<i>a</i>) ^a	– ^b
If	87 (<i>b</i>) ^a	66
Ig	35 (<i>a</i>) ^a , 59 (<i>b</i>) ^a	73

^a The procedure shown in Scheme 2 is indicated in parentheses.

^b The reaction led to the formation of an intractable mixture of products.

Thus we demonstrated that nitroalkanes are convenient precursors for previously unknown 6,7-dihydro-[1,2,3]triazolo[1,5-*a*]pyrazin-4-(5*H*)-ones.

EXPERIMENTAL

Catalytic hydrogenation was carried out in a steel pressure reactor (Pike instrument) equipped with a magnetic stirrer. NMR spectra were registered on a spectrometer Bruker AM-300. Chemical shifts were measured from the solvent signals used as internal reference [7]. The configuration of substituted oximes

III was derived from the data of ^1H and ^{13}C NMR spectra applying the rules described before (see, e.g., [8]). Elemental analyses were carried out in the microanalysis laboratory of the Institute of Organic Chemistry and in the analytical center of the Moscow Chemical Lycee. Melting points were measured on a Koeffler heating block and were reported without correction. TLC was performed on plates purchased from Merck (silica gel with QF-254 indicator). Spots were visualized under UV irradiation and/or using ninhydrin solution in ethanol. The preparative liquid chromatography was done on columns packed with silica gel Merck Kieselgel 60A 230-400 mesh.

Initial α -azidooximes **I** were obtained by published procedures [2].

General procedure of cycloaddition. a. Compounds IIIb, IIIc, IIIe, and IIIf. To a solution of 1 mmol of an appropriate α -azidooxime **I** in a mixture of 8 ml of water and 2 ml of acetonitrile was added 0.280 g (2 mmol) of ester **VIII**. The reaction mixture was stored for 96 h at room temperature with intermittent stirring, then it was poured into a mixture of 40 ml of ethyl acetate and 20 ml of water. The water layer was extracted with ethyl acetate (2 $\times$ 20 ml), the combined organic solvents were washed with water (2 $\times$ 20 ml), with a saturated NaCl solution (20 ml), and dried with Na_2SO_4 . The solvent was distilled off in a vacuum, the residue was purified by column chromatography on silica gel (**IIIb** and **IIIf**) (eluent hexane–AcOEt, 5:1 $\rightarrow$ 3:1) or by recrystallization from a mixture hexane–ethyl acetate (**IIIc** and **IIIe**).

b. Compounds IIIa, IIIc, IIIf, and IIIf. To a solution of 1 mmol of an appropriate α -azidooxime **I** in 2.5 ml of toluene was added 0.140 g (1 mmol) of ester **VIII**. The reaction mixture was stored for 72 h at room temperature with intermittent stirring. The solvent was distilled off in a vacuum, the residue was purified by column chromatography on silica gel (**IIIa** and **IIIf**) (eluent hexane–AcOEt, 5:1 $\rightarrow$ 13:1) or by recrystallization from a mixture hexane–ethyl acetate (**IIIc**).

Dimethyl 1-[2-(hydroximino)ethyl]-1H-1,2,3-triazole-4,5-dicarboxylate (IIIa). mp 97–99°C, R_f 0.15 (hexane–ethyl acetate, 1:1), isomers mixture *E* and *Z*, 1:1. *E*-isomer. ^1H NMR spectrum (DMSO- d_6), δ , ppm: 3.87 s, 3.90 s (6H, 2 Me), 5.37 d (2H, H_2C , J 4.3 Hz), 7.56 t (1H, CH, J 4.3 Hz), 11.34 br.s (1H, NOH). ^{13}C NMR spectrum (DMSO- d_6), characteristic signals, δ , ppm: 49.2 (CH_2), 52.7 and 53.6 (2 Me), 130.3 and 139.4 (C=C), 143.4 (C=N). *Z*-isomer. ^1H NMR spectrum

(DMSO- d_6), δ , ppm: 3.87 C, 3.90 C (6H, 2Me), 5.47 d (2H, H_2C , J 3.7 Hz), 7.00 t (1H, CH, J 3.7 Hz), 11.34 br.s (1H, NOH). ^{13}C NMR spectrum (DMSO- d_6), characteristic signals, δ , ppm: 46.0 (CH_2), 52.7 and 53.6 (2 Me), 130.3 and 139.4 (C=C), 143.6 (C=N). Unassigned signals of both isomers, ^{13}C , δ , ppm: 158.1, 158.2, 160.3 and 160.4 (2 CO_2Me). Found, %: C 40.02; H 4.29; N 22.86. $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_5$. Calculated, %: C 39.67; H 4.16; N 23.13.

Dimethyl 1-[2-(hydroximino)-1-methylpropyl]-1H-1,2,3-triazole-4,5-dicarboxylate (IIIb). Oily substance, R_f 0.27 (hexane–ethyl acetate, 1:1), isomers mixture *E* and *Z*, 3.2:1. *E*-isomer. ^1H NMR spectrum (DMSO- d_6), δ , ppm: 1.75 d (3H, CH_3CH , J 6.8 Hz), 3.87 s, 3.92 s (6H, 2 Me), 5.73 m (1H, H_3CCH), 7.60 d (1H, HC=N , J 3.9 Hz), 11.24 br.s (1H, NOH). ^{13}C NMR spectrum (DMSO- d_6), δ , ppm: 17.9 (CH_3CH), 56.1 (CH_3CH), 52.6 and 53.6 (2Me), 130.5 and 138.8 (C=C), 147.1 (C=N), 158.6 and 160.2 (2 CO_2Me). *Z*-isomer. ^1H NMR spectrum (DMSO- d_6), δ , ppm: 1.70 d (3H, CH_3CH , J 7.0 Hz), 3.87 s, 3.92 C (6H, 2 Me), 6.10 m (1H, H_3CCH), 7.07 d (1H, HC=N , J 5.4 Hz), 11.62 br.s (1H, NOH). ^{13}C NMR spectrum (DMSO- d_6), δ , ppm: 18.0 (CH_3CH), 51.2 (CH_3CH), 52.6 and 53.6 (2 Me), 130.4 and 138.5 (C=C), 146.9 (C=N), 158.6 and 160.2 (2 CO_2Me). Found, %: C 42.60; H 4.44; N 21.53. $\text{C}_9\text{H}_{12}\text{N}_4\text{O}_5$. Calculated, %: C 42.19; H 4.72; N 21.87.

Dimethyl 1-[2-(hydroximino)propyl]-1H-1,2,3-triazole-4,5-dicarboxylate (IIIc). mp 98–102°C, isomers mixture *E* and *Z*, 6.2:1. *E*-isomer. ^1H NMR spectrum (DMSO- d_6), δ , ppm: 1.79 s (3H, CH_3C), 3.88 s, 3.90 s (6H, 2Me), 5.36 s (2H, H_2C), 11.03 br.s (1H, NOH). ^{13}C NMR spectrum (DMSO- d_6), δ , ppm: 12.0 (CH_3C), 52.6 and 53.1 (2Me), 53.5 (CH_2), 130.7 and 139.1 (C=C), 149.8 (C=N), 158.2 and 160.3 (2 CO_2Me). *Z*-isomer. ^1H NMR spectrum (DMSO- d_6), δ , ppm: 1.58 s (3H, H_3CC), 3.88 s, 3.90 s (6H, 2Me), 5.48 s (2H, H_2C), 11.13 br.s (1H, NOH). ^{13}C NMR spectrum (DMSO- d_6), δ , ppm: 16.7 (CH_3C), 47.5 (CH_2), 52.6 and 53.1 (2 Me), 131.2 and 138.9 (C=C), 148.8 (C=N), 158.3 and 160.1 (2 CO_2Me). Found, %: C 42.24; H 4.61; N 21.75. $\text{C}_9\text{H}_{12}\text{N}_4\text{O}_5$. Calculated, %: C 42.19; H 4.72; N 21.87.

Dimethyl 1-[2-(hydroximino)-3-phenylpropyl]-1H-1,2,3-triazole-4,5-dicarboxylate (IIId). mp 77–78°C, isomers mixture *E* and *Z*, 5:1. *E*-isomer. ^1H NMR spectrum (DMSO- d_6), δ , ppm: 3.35 s (2H, H_2CPh), 3.77 s, 3.86 s (6H, 2Me), 5.32 s (2H, H_2CN), 7.14–7.38 m (5H, Ph), 11.32 br.s (1H, NOH). ^{13}C NMR spectrum (DMSO- d_6), δ , ppm: 31.8 (CH_2Ph), 51.7 and 52.6 (2 Me), 53.3 (CH_2N), 126.5, 128.6 and 128.8 (Ph), 135.5 (Ph^i), 130.7

and 139.2 (C=C), 151.0 (C=N), 157.9 and 160.2 (2 CO_2Me). *Z*-isomer. ^1H NMR spectrum ($\text{DMSO}-d_6$), δ , ppm: 3.35 s (2H, H_2CPh), 3.71 s, 3.82 s (6H, 2Me), 5.47 s (2H, H_2CN), 7.14–7.38 m (5H, Ph), 11.43 br.s (1H, NOH). ^{13}C NMR spectrum ($\text{DMSO}-d_6$), δ , ppm: 37.3 (CH_2Ph), 46.0 (CH_2N), 51.7 and 52.6 (2Me), 126.6, 128.3 and 128.4 (Ph), 135.6 (Ph^i), 130.7 and 139.9 (C=C), 150.5 (C=N), 157.9 and 160.1 (2 CO_2Me). Found, %: C 54.29; H 4.71; N 16.93. $\text{C}_{15}\text{H}_{16}\text{N}_4\text{O}_5$. Calculated, %: C 54.21; H 4.85; N 16.86.

Dimethyl 1-[2-(hydroximino)-1-methyl-3-methoxy-3-oxopropyl]-1*H*-1,2,3-triazole-4,5-dicarboxylate (IIIe). mp 140–145°C. ^1H NMR spectrum ($\text{DMSO}-d_6$), δ , ppm: 1.90 d (3H, H_3CCH , J 6.8 Hz), 3.68 s (3H, $\text{H}_3\text{CO}_2\text{CC}=\text{N}$), 3.85 s, 3.86 s (6H, 2Me), 6.19 q (1H, H_3CCH , J 6.8 Hz), 12.91 br.s (1H, NOH). ^{13}C NMR spectrum ($\text{DMSO}-d_6$), δ , ppm: 15.6 (CH_3CH), 52.3, 52.5, 52.7 and 53.5 (3 CO_2Me and CH_3CH), 130.4 and 138.8 (C=C), 147.0 (C=N), 158.4 and 160.2 (2 CO_2Me), 162.1 ($\text{H}_3\text{CO}_2\text{CC}=\text{N}$). Found, %: C 42.43; H 4.43; N 17.58. $\text{C}_{11}\text{H}_{14}\text{N}_4\text{O}_7$. Calculated, %: C 42.04; H 4.49; N 17.83.

Dimethyl 1-[3-hydroxy-2-(hydroximino)-propyl]-1*H*-1,2,3-triazole-4,5-dicarboxylate (III*f*). mp 128–136°C, R_f 0.06 (hexane–ethyl acetate, 1:1), isomers mixture *E* and *Z*, 3.1:1. *E*-isomer. ^1H NMR spectrum ($\text{DMSO}-d_6$), δ , ppm: 3.00 br.s (1H, OH), 3.93 s, 3.97 s (6H, 2Me), 4.05 s (2H, H_2CO), 5.59 s (2H, H_2CN), 9.87 br.s (1H, NOH). ^{13}C NMR spectrum ($\text{DMSO}-d_6$), δ , ppm: 44.9 (CH_2N), 52.9 and 53.7 (2Me), 61.1 (CH_2O), 131.3 and 139.3 (C=C), 152.0 (C=N), 158.7 and 160.3 (2 CO_2Me). *Z*-isomer. ^1H NMR spectrum ($\text{DMSO}-d_6$), δ , ppm: 3.00 br.s (1H, HO), 3.93 s, 3.97 s (6H, 2Me), 4.50 s (2H, H_2CO), 5.48 s (2H, H_2CN), 9.40 br.s (1H, NOH). ^{13}C NMR spectrum ($\text{DMSO}-d_6$), δ , ppm: 49.9 (CH_2N), 52.9 and 53.6 (2 Me), 57.0 (CH_2O), 131.0 and 139.3 (C=C), 155.1 (C=N), 158.7 and 160.3 (2 CO_2Me). Found, %: C 39.94; H 4.56; N 20.31. $\text{C}_9\text{H}_{12}\text{N}_4\text{O}_6$. Calculated, %: C 39.71; H 4.44; N 20.58.

Dimethyl 1-[2-(hydroximino)-5-(methyloxy)-5-oxopentyl]-1*H*-1,2,3-triazole-4,5-dicarboxylate (III*g*). Oily substance, R_f 0.25 (hexane–ethyl acetate, 1:1), isomers mixture *E* and *Z*, 2.6:1. *E*-isomer. ^1H NMR spectrum ($\text{DMSO}-d_6$), δ , ppm: 2.47–2.64 m (4H, $\text{H}_2\text{CCH}_2\text{CO}_2\text{Me}$ and $\text{H}_2\text{CCH}_2\text{CO}_2\text{Me}$), 3.63 s, 3.89 s (9H, 3Me), 5.47 s (2H, H_2CN), 11.17 br.s (1H, HON). ^{13}C NMR spectrum ($\text{DMSO}-d_6$), characteristic signals, δ , ppm: 21.9 ($\text{CH}_2\text{CH}_2\text{CO}_2\text{Me}$), 28.9 ($\text{CH}_2\text{CH}_2\text{CO}_2\text{Me}$), 52.1 (CH_2N), 130.8 and 139.2 (C=C), 151.8 (C=N), 158.2 and 160.3 (2 CO_2Me), 172.6 ($\text{CH}_2\text{CH}_2\text{CO}_2\text{Me}$). *Z*-isomer.

^1H NMR spectrum ($\text{DMSO}-d_6$), δ , ppm: 2.47–2.64 m (4H, $\text{H}_2\text{CCH}_2\text{CO}_2\text{Me}$ and $\text{H}_2\text{CCH}_2\text{CO}_2\text{Me}$), 3.56 s, 3.93 s (9H, 3Me), 5.73 s (2H, H_2CN), 11.34 br.s (1H, HON). ^{13}C NMR spectrum ($\text{DMSO}-d_6$), characteristic signals, δ , ppm: 26.1 ($\text{CH}_2\text{CH}_2\text{CO}_2\text{Me}$), 29.1 ($\text{CH}_2\text{CH}_2\text{CO}_2\text{Me}$), 46.8 (CH_2N), 131.2 and 138.8 (C=C), 150.0 (C=N), 158.3 and 160.1 (2 CO_2Me), 172.4 ($\text{CH}_2\text{CH}_2\text{CO}_2\text{Me}$). Unassigned signals of both isomer, ^{13}C NMR spectrum, δ , ppm: 51.3, 51.5, 52.1, 52.6, 53.4, 53.6 and 54.8 [3Me and CH_2N (*E*-isomer)]. Found, %: C 44.25; H 5.07; N 16.63. $\text{C}_{12}\text{H}_{16}\text{N}_4\text{O}_7$. Calculated, %: C 43.90; H 4.91; N 17.07.

Dimethyl 1-(2-oxopropyl)-1*H*-1,2,3-triazole-4,5-dicarboxylate (IV*c*) was isolated as a side product from the reaction mixture obtained from oxime **Ic** and ester **VIII** by procedure *a* in a mixture with heterocycle **IIIc**. R_f 0.14 (hexane–ethyl acetate, 1:1). Identified by NMR data. ^1H NMR spectrum (CDCl_3), δ , ppm: 2.29 s (3H, H_3C), 3.86 s, 3.89 s (6H, 2Me), 5.73 s (2H, H_2C). ^{13}C NMR spectrum (CDCl_3), δ , ppm: 27.0 (CH_3), 52.6 and 53.3 (2Me), 59.0 (CH_2), 130.0 and 139.4 (C=C), 157.9 and 160.3 (2 CO_2Me), 199.8 (C=O).

c. Hydrogenation of oximes III. To a solution of 1 mmol of an appropriate oxime **III** in 2.5 ml of methanol was added ~0.05 of Raney nickel in methanol. The mixture was hydrogenated for 2 h at 70–80°C and hydrogen pressure 80 at, then the catalyst was filtered off, and the solvent was distilled off in a vacuum. The reaction product was recrystallized from a mixture ethyl acetate–methanol.

Methyl 4-oxo-4,5,6,7-tetrahydro[1,2,3]triazolo[1,5-*a*]pyrazine-3-carboxylate (II*a*). mp 220–228°C. ^1H NMR spectrum ($\text{DMSO}-d_6$), δ , ppm: 3.70 m (2H, H_2CNH), 3.86 s (3H, Me), 4.66 t (2H, H_2CN , J 5.8 Hz), 8.64 br.s (1H, HN). ^{13}C NMR spectrum (CDCl_3), δ , ppm: 38.7 and 45.5 (CH_2NH and CH_2N), 52.3 (Me), 129.5 and 138.1 (C=C), 155.4 (CONH), 160.6 (CO_2Me). Found, %: C 43.06; H 4.09; N 27.87. $\text{C}_7\text{H}_8\text{N}_4\text{O}_3$. Calculated, %: C 42.86; H 4.11; N 28.56.

Methyl 7-methyl-4-oxo-4,5,6,7-tetrahydro[1,2,3]triazolo[1,5-*a*]pyrazine-3-carboxylate (II*b*). mp 195–198°C. ^1H NMR spectrum ($\text{DMSO}-d_6$), δ , ppm: 1.60 d (3H, H_3CCH , J 6.3 Hz), 3.44 d.d (1H, HCNH , J 8.7, 13.5 Hz), 3.68 m (1H, HCNH), 3.85 s (3H, Me), 4.90 m (1H, H_3CCH , J 6.3 Hz), 8.62 br.s (1H, HN). ^{13}C NMR spectrum (CDCl_3), δ , ppm: 16.0 (CH_3CH), 44.6 (CH_2NH), 52.3 and 52.7 (CH_3CH and Me), 129.0 and 138.5 (C=C), 155.3 (CONH), 160.7 (CO_2Me). Found, %: C 45.88; H 4.58; N 26.78. $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_3$. Calculated, %: C 45.71; H 4.80; N 26.66.

Methyl 6-methyl-4-oxo-4,5,6,7-tetrahydro[1,2,3]-triazolo[1,5-*a*]pyrazine-3-carboxylate (IIc). mp 228–232°C. ^1H NMR spectrum ($\text{DMSO-}d_6$), δ , ppm: 1.23 d (3H, H_3CCH , J 6.1 Hz), 3.85 s (3H, Me), 4.05 m (1H, H_3CCH), 4.32 d.d (1H, HC–N, J 9.8, 12.8 Hz), 4.80 d.d (1H, HC–N, J 3.7, 12.8 Hz), 8.72 br.s (1H, HN). ^{13}C NMR spectrum (CDCl_3), δ , ppm: 17.5 (CH_3CH), 46.0 (CH_3CH), 50.7 (CH_2N), 52.4 (Me), 129.1 and 138.0 (C=C), 155.1 (CONH), 160.6 (CO_2Me). Found, %: C 45.60; H 4.55; N 26.43. $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_3$. Calculated, %: C 45.71; H 4.80; N 26.66.

Methyl 6-benzyl-4-oxo-4,5,6,7-tetrahydro[1,2,3]-triazolo[1,5-*a*]pyrazine-3-carboxylate (IIId). mp 184–188°C. ^1H NMR spectrum ($\text{DMSO-}d_6$), δ , ppm: 2.76 d.d (1H, CHPh, J 7.3, 14.0 Hz), 2.93 d.d (1H, CHPh, J 5.2, 14.0 Hz), 3.82 s (3H, Me), 4.20 m (1H, HCNH), 4.52 m (2H, H_2CN), 7.14–7.41 m (5H, Ph), 8.79 br.s (1H, HN). ^{13}C NMR spectrum (CDCl_3), δ , ppm: 38.3 (CH_2Ph), 48.5 and 50.6 (CHNH and CH_2N), 52.3 (Me), 129.1 and 137.9 (C=C), 126.8, 128.5 and 129.3 ($\text{Ph}^{o,m,p}$), 136.1 (Ph^i), 155.4 (CONH), 160.5 (CO_2Me). Found, %: C 58.68; H 4.90; N 19.29. $\text{C}_{14}\text{H}_{14}\text{N}_4\text{O}_3$. Calculated, %: C 58.73; H 4.93; N 19.57.

Methyl 6-(hydroxymethyl)-4-oxo-4,5,6,7-tetrahydro[1,2,3]triazolo[1,5-*a*]pyrazine-3-carboxylate (IIIf). mp 189–191°C. ^1H NMR spectrum ($\text{DMSO-}d_6$), δ , ppm: 3.29–3.43 m (2H, HO and HC–N), 3.53 m (1H, HC–N), 3.85 s (3H, Me), 4.70 m (2H, H_2CO), 5.15 m (1H, HCNH), 8.64 br.s (1H, HN). ^{13}C NMR spectrum (CDCl_3), δ , ppm: 46.4 and 52.3 (HCNH and H_2CN), 51.2 (Me), 61.3 (CH_2O), 129.2 and 137.8 (C=C), 155.0 (CONH), 160.6 (CO_2Me). Found, %: C 42.27; H 4.52; N 24.50. $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_4$. Calculated, %: C 42.48; H 4.46; N 24.78.

Methyl 6-(3-methoxy-3-oxopropyl)-4-oxo-4,5,6,7-tetrahydro[1,2,3]triazolo[1,5-*a*]pyrazine-3-carboxylate

(IIIg). mp 160–164°C. ^1H NMR spectrum ($\text{DMSO-}d_6$), δ , ppm: 1.81 d.d (2H, $\text{H}_2\text{CCH}_2\text{CO}_2\text{Me}$, J 7.3, 14.4 Hz), 2.48 m (2H, $\text{H}_2\text{CCH}_2\text{CO}_2\text{Me}$), 3.60 s, 3.86 s (6H, 2Me), 3.95 m (1H, HCNH), 4.49 d.d (1H, HC–N, J 7.6, 13.5 Hz), 4.81 d.d (1H, HC–N, J 4.2, 13.5 Hz), 8.79 br.s (1H, HN). ^{13}C NMR spectrum (CDCl_3), δ , ppm: 27.0 and 29.1 ($\text{CH}_2\text{CH}_2\text{CO}_2\text{Me}$ and $\text{CH}_2\text{CH}_2\text{CO}_2\text{Me}$), 49.1 and 49.3 (CHNH and $\text{CH}_2\text{CH}_2\text{CO}_2\text{Me}$), 51.5 and 52.3 (CH_2N and CO_2Me), 129.0 and 137.9 (C=C), 154.9 (CONH), 160.5 (2 CO_2Me). Found, %: C 46.53; H 4.96; N 19.81. $\text{C}_{11}\text{H}_{14}\text{N}_4\text{O}_5$. Calculated, %: C 46.81; H 5.00; N 19.85.

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