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A Convenient Synthesis of 3,6-Disubstituted-1,4-Dihydro-[1,2,4,5]Tetrazines and Preparation of New Acetic Acid Derivatives Containing 5-Oxo-4-Phenylamino-4,5-Dihydro-[1,2,4]Triazole

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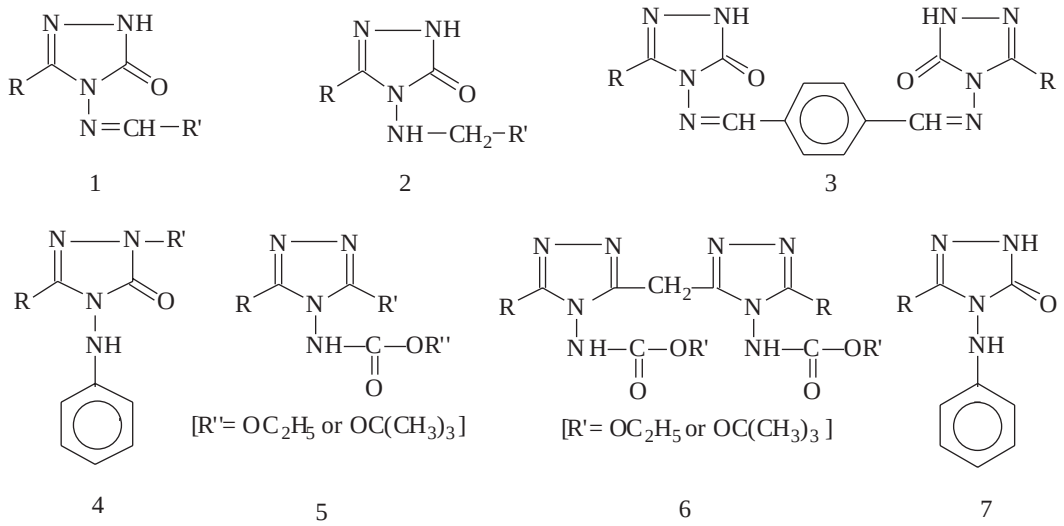
A series of compounds **8a-e,** was synthesized by condensation of compounds **7a-e** with ethyl bromoacetate. The treatment of compounds **8a-e** with hydrazine hydrate afforded the corresponding hydrazide derivatives (**9a-e**). Subsequently, compounds **9a-e** were converted to alkylidene hydrazides (**10a-e**). Moreover, upon heating in the presence of carboxylic acids, compounds **9a-e** unexpectedly gave 1,4-dihydro-[1,2,4,5]tetrazine derivatives (**11a-e**).

Key Words: Conformer, geometrical isomer, ethyl bromoacetate, imine bond, 5-oxo-[1,2,4]triazole, [1,2,4,5]tetrazine.

Introduction

Compounds containing imine bond have been intensively synthesized for various reasons, one of which is their biological activities[1−4]. Some of the other reasons are the investigation of their ability to make a coordination complex with transition metal cations and the improvement of their properties for analytical applications[5−7]. In addition, there exist a number of compounds incorporating [1,2,4]triazole, 5-oxo-[1,2,4]triazole or 5-thioxo-[1,2,4]triazole rings and having diverse biological activities,[1−3,8−25] some of which have a group also contains an imine bond[1−3]. Among these compounds, 3-alkyl-4-alkylidene(or alkyl)amino-5-oxo-4,5-dihydro-[1.2.4]triazoles (**1**,**2**), *N*, *N′*-bis-(3-alkyl-5-oxo-4,5-dihydro-[1,2,4]triazol-4-yl)-1,4-xylenediimines (**3**), 1,3-dialkyl-4-phenylamino-5-oxo-4,5-dihydro-[1,2,4]triazoles (**4**), 3,5-dialkyl-4-ethoxy(*t*-butoxy)carbonyl-amino-4H-[1,2,4]triazoles (**5**) and di-(3-alkyl-4-ethoxy(*t*-butoxy)carbonylamino-4H-[1,2,4]triazol-5-yl)-methanes (**6**) were synthesized in our laboratories (figure)[1,8,9,12−14,26,27]. In addition, several [1,2,4]triazole derivatives obtained as potential biologically active compounds[28,29].



Figure

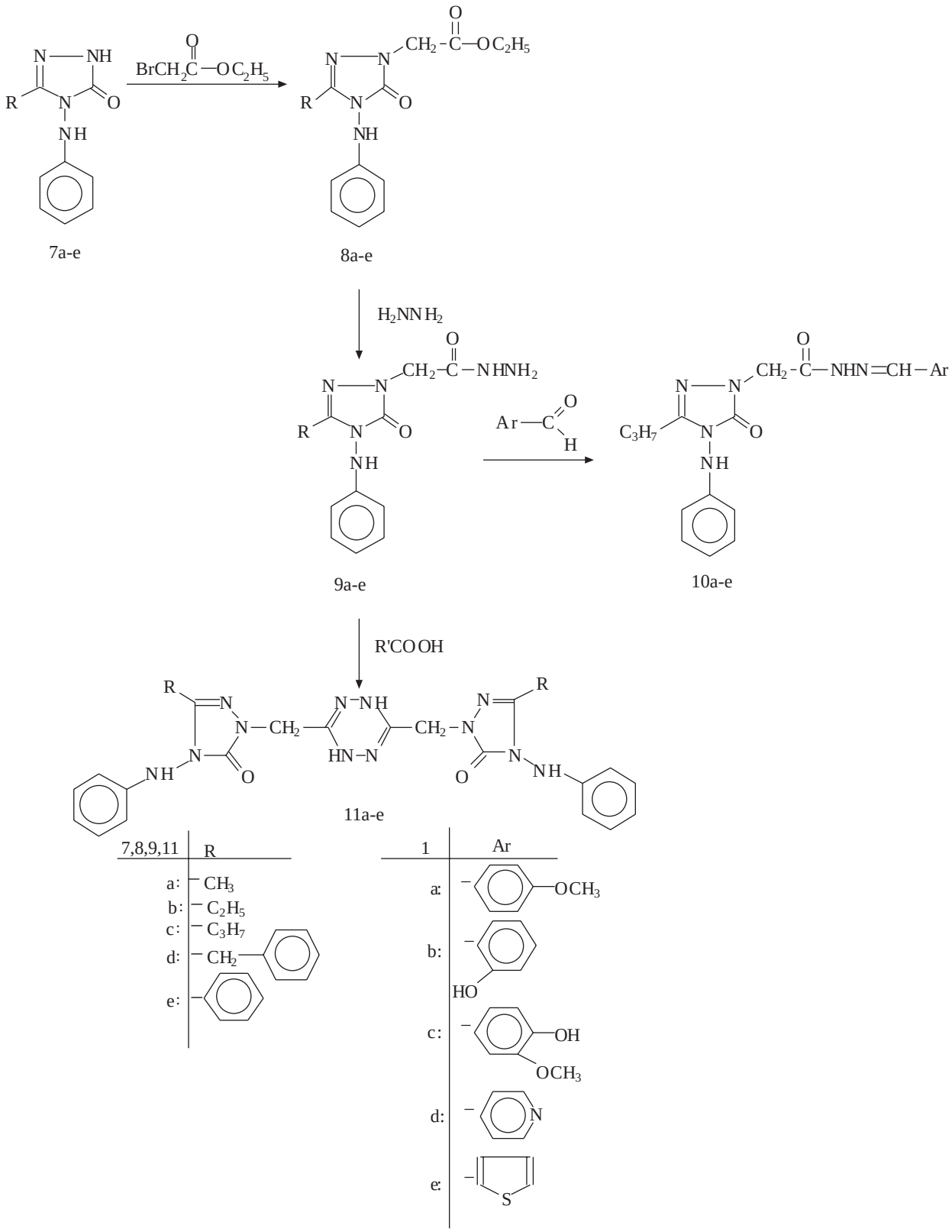
The chemistry of 3-alkyl-5-oxo-4-phenylamino-4,5-dihydro-[1,2,4]-triazole compounds (**7**), which behave as good nucleophiles in most reactions, has been studied in detail. For example, the bromination, nitration and alkylation of these compounds have been performed in our laboratories[12,13,30].

Results and Discussion

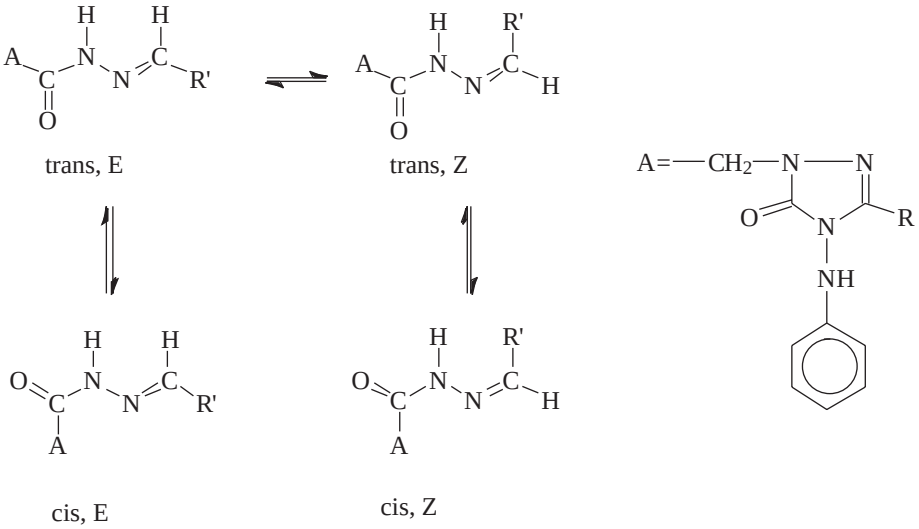
In line with our continuing interest, we aimed to obtain possible biologically active compounds containing a 5-oxo-4-phenylamino-4,5-dihydro-1H-[1,2,4]triazole ring bearing a side chain incorporating an imine bond. For this purpose, compounds **8** were obtained via a nucleophilic attack of compounds **7,** which were obtained from the reaction of the ester ethoxycarbonylhydrazones with phenyl hydrazine[33] to the bromide-bearing carbon of ethyl bromoacetate. After that, compounds **8a-e** were converted to their hydrazide derivatives (**9a-e**) by treating them with hydrazine hydrate. 3-Alkyl-5-oxo-4-phenylamino-4,5-dihydro [1,2,4]triazol-1-yl-acetic acid arylidenehydrazides (**10a-e**) were synthesized by the reaction of compounds **9a-e** with various aldehydes such as salicylaldehyde, anisaldehyde, vanillin, pyridine-4-carboxaldehyde and thiophene-2-carboxaldehyde. The heating of compounds **9a-e** in the presence of carboxylic acids such as acetic or benzoic acids resulted in the formation of 1,4-dihydro-[1,2,4,5]tetrazine derivatives (**11a-e**) (Scheme 1).

In the ^{1}H NMR spectra of compounds **8a-e** no signal belonging to the endocyclic-NH proton of compounds **7a-e** was observed. Instead, new signals belonging to the ethyl ester group appeared between 4.77 and 4.16 ppm (-O$\underline{CH_2}$CH$_3$), 4.16 and 4.19 ppm (-NCH$_2$) and 1.21 and 1.23 ppm (-OCH$_2\underline{CH_3}$). The signals of corresponding carbons were recorded between 60.94 and 64.92 ppm (-O$\underline{CH_2}$CH$_3$), 46.70 and 50.75 ppm (-NCH$_2$) and 13.92 and 17.60 ppm (-OCH$_2\underline{CH_3}$) in the ^{13}C NMR spectra. When compounds **8a-e** were converted to their hydrazides (**9a-e**), these signals, except for the signal belonging to –NCH$_2$- dissappeared in the ^{1}H and ^{13}C NMR spectra. Instead, new signals belonging to the hydrazide group were observed between 8.93 and 9.24 ppm (-$\underline{NH}$NH$_2$) and 4.30 and 4.35 ppm (-NH$\underline{NH_2}$) (checked by exchanging with D$_2$O).

It has been reported that the compounds incorporating an arylidene (or alkylidene) hydrazide structure may exist as *Z*/*E* geometrical isomers about a -C=N- double bond. Moreover, *Z* and *E* isomers may consist of their individual *cis-trans* amide conformers[2,4–6] (Scheme 2). According to the literature[2,4], the



Scheme 1. Synthetic pathway for the preparation of compounds **8-11**.

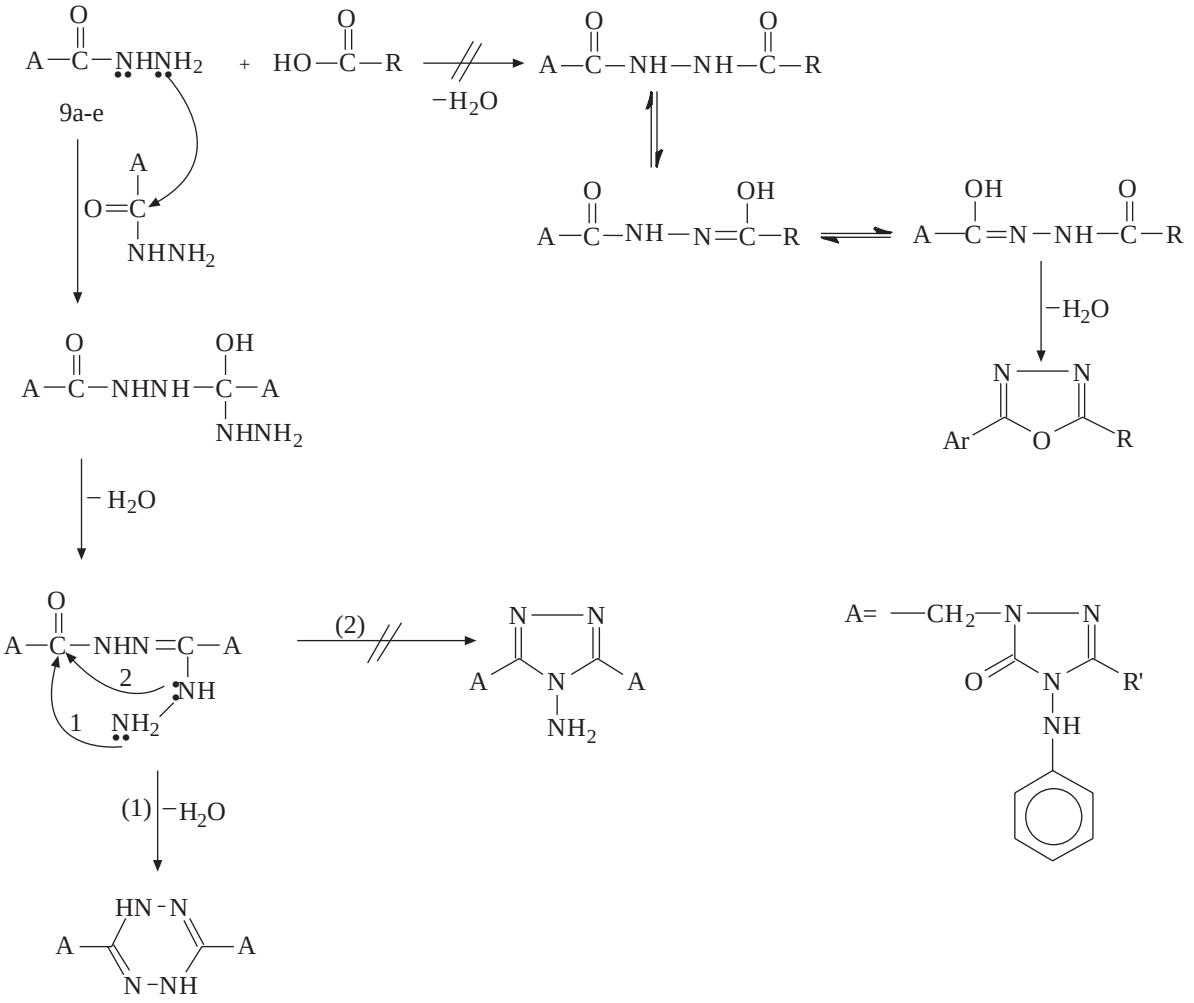


Scheme 2. *E/Z* geometrical isomers and *cis/trans* conformers in compounds **10a-e**.

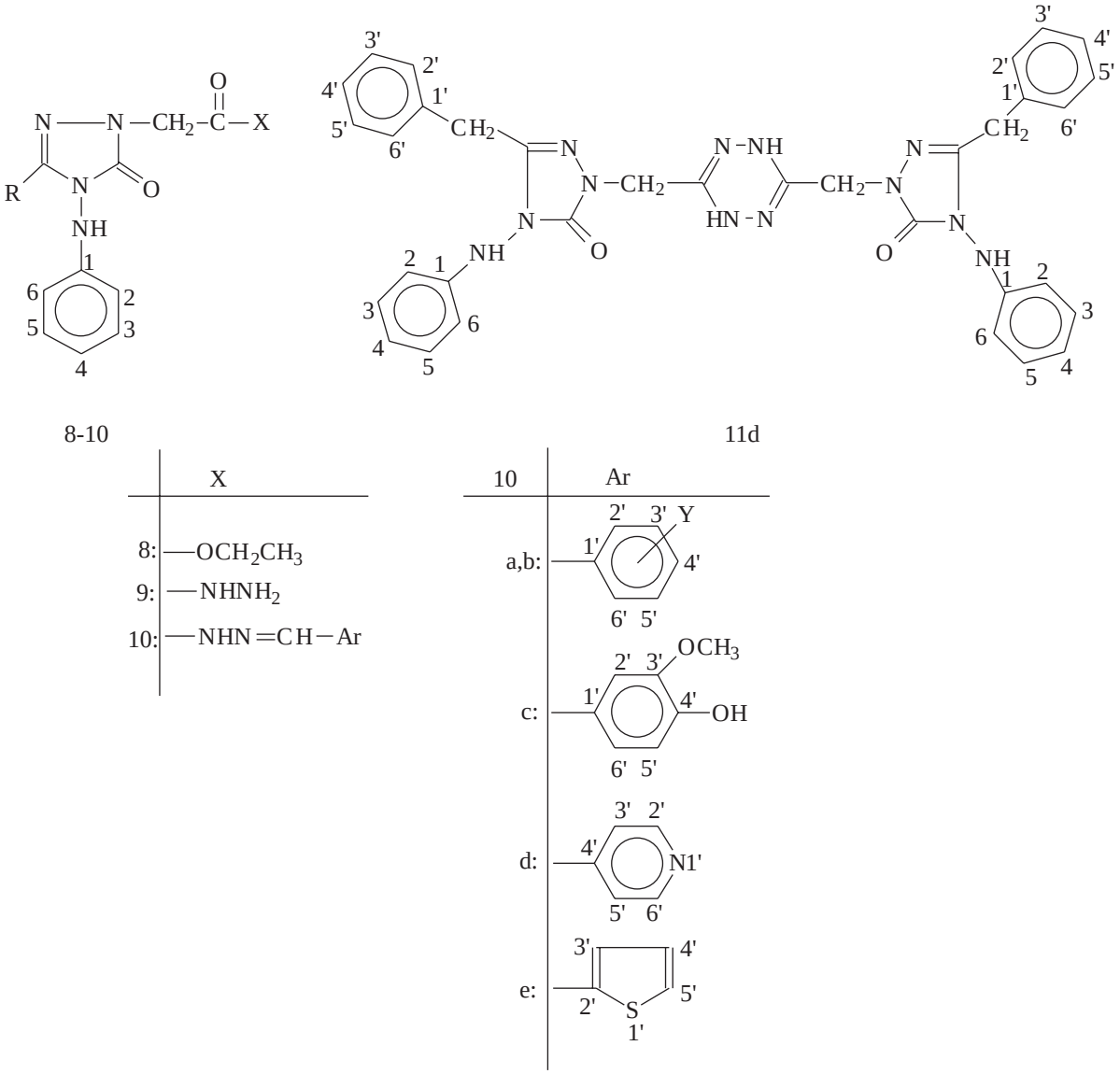
compounds containing imine bonds are present in higher percentages in dimethyl-d_6 sulfoxide solution in the form of a geometric *E* isomer about a -C=N double bond. The *Z* isomers can be stabilized in less polar solvents by an intramolecular hydrogen bond[6]. In the present study, the stereochemical behavior of compounds **10a-e**, which were obtained by using various aldehydes, was investigated in dimethyl-d_6 sulfoxide solution as *E* isomers and the *trans/cis* conformer ratios in each case were calculated by using ^{1}H NMR and ^{13}C NMR data. In the ^{1}H NMR spectra of compounds **10a-e**, 2 sets of signals each belonging to the individual –NCH_2, N=CH, hydrazide-NH and -OH (for **10b** and **10c**), of the *cis* and *trans* conformers were observed. Among these, the peaks belonging to the –NCH_2 group of 1 of 2 conformers of each compound **10** appeared at about 4.44-4.53 ppm, while the –NCH_2 peaks belonging to the other conformer appeared between 4.81 and 4.93 ppm. The –N=CH signals were observed as separate peaks for each conformer at 7.94-8.39 and 8.05-8.44 ppm. For hydrazide-NH 2 peaks were recorded at about 11.38-11.69 ppm and 11.41-11.96 ppm indicating *trans* and *cis* conformers of compounds **10a-e**. In the case of compounds **10b** and **10c**, 2 signals belonging to the –OH group were recorded between 9.53 and10.06 ppm and 9.59 and10.96 ppm, respectively. In the ^{13}C NMR spectra of compounds **10a-e**, each signal belonging to the triazole-C-5, triazole-C-3, -N=CH and -NCH_2 groups was observed as 2 sets, indicating the formation of conformational isomers. In the present study, the *trans/cis* ratio changed between 71/29 and 57/43 in the mixture of the conformers. When D_2O was added to the DMSO-d_6 solution of compounds **10a-e**, the *trans/cis* ratio changed between 58/42 and 42/58. This change is evidence of the exsistence of *trans/cis* conformers, not *E/Z* geometrical isomers, since *E/Z* isomers are rigid structures.

The formation of [1,3,4]oxadiazoles from the reaction of the compounds having a hydrazide structure with carboxylic acids was carried out[32]. In addition, it has been reported that the reaction of dicarboxilic acids with hydrazine hydrate resulted in the formation of a polymer containing a [1,3,4]oxadiazole ring[33]. When compounds **9a-e** were treated with acetic acid or benzoic acid to obtain [1,3,4]oxadiazoles, the reaction surprisingly resulted in the formation of 1,4-dihydro-[1,2,4,5]tetrazine derivatives. It could be concluded that in the first step of this reaction a dimerization took place between 2 molecules of compounds **9a-e** instead of a reaction with carboxylic acid. In the second step of this reaction, although there were 2 possibilities, the

formation of either 4-amino-[1,2,4]triazole or [1,2,4,5]tetrazine derivative, we expected to obtain 4-amino-[1,2,4]triazole derivatives due to the instability of tetrazines (Scheme 3). It has been reported that tetrazines are generally unstable and are converted to [1,2,4]triazole derivatives or decomposed upon heating above 100 °C[33,34]. Moreover, it has been reported that if there are 2 possibilities such as in the above case, 4-amino-[1,2,4]triazoles are obtained as the main product[26]. In contrast to the literature, the tetrazine derivatives (**11a-e**) were obtained at a high yield in this study. In the NMR spectra of compounds **11a-e,** the absence of any signal belonging to the $-CH_3$ or $-C_6H_5$ groups derived from the carboxylic acid used in the reaction indicated that compounds **9a-e** did not react with carboxylic acids. In addition, in the ^{1}H NMR spectra of compounds **11a-e**, the additional signal belonging to tetrazine–NH protons was at 10.35 ppm (D_2O exch.), while the hydrazide-NH_2 observed at 4.29 ppm disappeared. ^{13}C NMR signals of C-3 and C-6 of compounds **11a-e** were recorded at 163.28-165.21 ppm. In the IR spectra of compounds **11a-e** additional –NH signals belonging to the tetrazine ring were observed at 3130-3132 cm^{-1} while the peak belonging to hydrazide-NH_2 disappeared. Moreover, in the IR and NMR spectra of the tetrazines (**11a-e**), no signal representing an $-NH_2$ group derived from the 3,5-dialkyl-4-amino-[1,2,4]triazole structure was observed. Furthermore, elemental analysis confirmed all the structures proposed in this study.



Scheme 3. The formation mechanism of compounds **11a-e**.



Scheme 4. The numbers of aromatic atoms on compounds **8-11** (Y: -OH or OCH3).

Experimental

Melting points were determined on a Gallenkamp melting point apparatus and are uncorrected. ^{1}H, ^{13}C, APT and DEPT NMR spectra were recorded on a Varian-Mercury 200 MHz spectrometer. The IR spectra were measured as potassium bromide pellets using a Perkin-Elmer 1600 series FTIR spectrophotometer. Combustion analysis was performed on a Carlo Erba 1106 elemental analyzer. All the chemicals were obtained from Fluka Chemie AG Buchs (Switzerland). The precursor compounds **7a-e** were synthesized according to the published method[33].

General method for the synthesis of compounds 8

The corresponding 3-alkyl-4-phenylamino-4,5-dihydro-1H-1,2,4-triazol-5-one (**1**) (0.01 mol) was refluxed with an equivalent amount of natrium in absolute ethanol for 2 h. Then, ethyl bromoacetate (0.01 mol) was added and refluxed for an additional 5 h. After evaporation at 35-40 ° C under reduced pressure, a solid appeared. This was recrystallized from an appropriate solvent to afford the desired compound.

3-Methyl-5-oxo-4-phenylamino-4,5-dihydro-[1,2,4]triazol-1-yl-acetic acid ethyl ester (8a): Recrystallization from isobutyl acetate (yield: 82.20%), mp. 125-126 °C; Analysis (Calc/found %): for $C_{13}H_{16}O_3N_4$ C: 56.51/56.55, H: 5.84/5.97, N: 20.28/19.78; IR (KBr) (ν, cm^{-1}), 3252 (-NH), 1760 (ester -C=O), 1715 (triazole -C=O), 1597 (-C=N), 1215 (-C-O); ^{1}H NMR (DMSO-d_6) δ 1.21 (t, -OCH$_2$<u>CH$_3$</u>, J = 7.0 Hz), 2.09 (s, -CH$_3$), 4.19 (q, -O<u>CH$_2$</u>CH$_3$, J = 7.0 Hz), 4.76 (s, -NCH$_2$), [ar H: 6.57 (d, 2H, CH-2, CH-6, J = 8.2 Hz), 6.86 (t, 1H, CH-4, J = 7.6 Hz), 7.23 (t, 2H, CH-3, CH-5, J = 7.6 Hz)], 9.03 (s, -NH); ^{13}C NMR (DMSO-d_6) δ 167.82 (C=O), 152.20 (triazole-C-5), 145.49 (triazole C-3), [ar C: 146.38 (C-1), 129.18 (C-3, C-5), 120.29 (C-4), 111.94 (C-2, C-6)], 63.13 (-O<u>CH$_2$</u>CH$_3$), 46.63 (-NCH$_2$), 13.92 (-OCH$_2$<u>CH$_3$</u>), 10.32 (-CH$_3$).

3-Ethyl-5-oxo-4-phenylamino-4,5-dihydro-[1,2,4]triazol-1-yl-acetic acid ethyl ester (8b): Recrystallization from isobutyl acetate (yield: 78.90%), mp. 121-122 °C; Analysis (Calc/found %): for $C_{14}H_{18}O_3N_4$ C: 57.92/57.52, H: 6.25/6.67, N: 19.30/19.68; IR (KBr) (ν, cm^{-1}), 3255 (NH), 1761 (ester C=O), 1711 (triazole-C=O), 1587 (-C=N), 1210 (-C-O); ^{1}H NMR (DMSO-d_6) δ 1.11 (t, -CH$_2$<u>CH$_3$</u>, J =7.5 Hz), 1.21 (t, -OCH$_2$<u>CH$_3$</u>, J = 7.1 Hz), 2.48 (q, -<u>CH$_2$</u>CH$_3$, J = 7.5 Hz), 4.18 (q, -O<u>CH$_2$</u>CH$_3$, J = 7.1 Hz), 4.76 (s, -NCH$_2$), [ar H: 6.59 (d, 2H, CH-2, CH-6, J = 8.2 Hz), 6.81 (t, 1H, CH-4, J = 7.4 Hz), 7.23 (t, 2H, CH-3, CH-5, J = 7.8 Hz)], 9.03 (s, -NH); ^{13}C NMR (DMSO-d_6) δ 167.81 (-C=O), 152.20 (triazole C-5), 149.35 (triazole C-3), [ar C: 146.35 (C-1), 129.14 (C-3, C-5), 120.22 (C-4), 111.92 (C-2, C-6)], 63.13 (-O<u>CH$_2$</u>CH$_3$), 46.70 (-NCH$_2$), 17.91 (-<u>CH$_2$</u>CH$_3$), 13.92 (-OCH$_2$<u>CH$_3$</u>), 9.87 (-CH$_2$<u>CH$_3$</u>).

5-Oxo-4-phenylamino-3-n-propyl-4,5-dihydro-[1,2,4]triazol-1-yl-acetic acid ethyl ester (8c): Recrystallization from benzene-petroleum ether (1:2) (yield: 70.43%), mp. 81-83 °C; Analysis (Calc/found %): for $C_{15}H_{20}O_3N_4$ C: 59.20/58.51, H: 6.62/6.59, N: 18.41/19.18; IR (KBr) (ν, cm^{-1}), 3245 (NH), 1760 (ester -C=O), 1708 (triazole-C=O), 1585 (-C=N), 1209 (-C-O); ^{1}H NMR ($CDCl_3$) δ 0.94 (t, -CH$_2$CH$_2$<u>CH$_3$</u>, J =7.0 Hz), 1.29 (t, -OCH$_2$<u>CH$_3$</u>, J = 7.6 Hz), 1.68 (m, -CH$_2$<u>CH$_2$</u>CH$_3$), 2.50 (t, -<u>CH$_2$</u>CH$_2$CH$_3$, J =7.0 Hz), 4.18 (q, -O<u>CH$_2$</u>CH$_3$, J =7.4 Hz), 4.77 (s, -NCH$_2$), [ar H: 6.57 (d, 2H, CH-2, CH-6, J = 7.4 Hz), 6.92 (t, 1H, CH-4, J = 7.0 Hz), 7.17 (t, 2H, CH-3, CH-5, J = 7.2 Hz)], 7.52 (s, -NH); ^{13}C NMR ($CDCl_3$) δ 167.58 (C=O), 153.50 (triazole C-5), 149.29 (triazole C-3), [ar C: 145.56 (C-1), 129.31 (C-3, C-5), 121.57 (C-4), 112.81 (C-2, C-6)], 61.80 (-O<u>CH$_2$</u>CH$_3$), 47.01 (-NCH$_2$), 26.81 (-<u>CH$_2$</u>CH$_2$CH$_3$), 19.28 (-CH$_2$<u>CH$_2$</u>CH$_3$), 14.09(-OCH$_2$<u>CH$_3$</u>), 13.55 (-CH$_2$CH$_2$<u>CH$_3$</u>).

3-Benzyl-5-Oxo-4-phenylamino-4,5-dihydro-[1,2,4]triazol-1-yl-acetic acid ethyl ester (8d): Recrystallization from benzene-petroleum ether (1:2) (yield: 58.40%), mp. 86-88 °C; Analysis (Calc/found %): for $C_{19}H_{20}O_3N_4$C: 64.76/65.59, H: 5.72/5.47, N: 15.90/15.93; IR (KBr) (ν, cm^{-1}), 3252 (NH), 1765 (ester-C=O), 1704 (triazole-C=O), 1640 (-C=N), 1215 (-C-O); ^{1}H NMR (DMSO-d_6) δ 1.21 (t, -OCH$_2$<u>CH$_3$</u>, J = 7.6 Hz), 2.48 (s, benzyl-<u>CH$_2$</u>), 4.16 (q, -O<u>CH$_2$</u>CH$_3$, J = 7.6 Hz), 4.61 (s, -NCH$_2$), [ar H: 6.64 (bs, 2H, CH-2, CH-6), 6.86 (t, 1H, CH-4, J = 7.4 Hz), 7.23 (t, 2H, CH-3, CH-5, J = 7.8 Hz), 7.30-7.45 (m, 5H)],

9.03 (s, -NH); ^{13}C NMR (DMSO-d_6) δ 170.05 (-C=O), 153.70 (triazole C-5), 148.70 (triazole C-3), [ar C: 147.40 (C-1), 134.10 (C-1'), 131.35 (C-3', C-5'), 129.01 (C-3, C-5), 128.20 (C-2', C-6'), 126.05 (C-4'), 124.01 (C-4), 116.45 (C-2, C-6),], 60.94 (-O<u>CH$_2$</u>CH$_3$), 46.20 (-NCH$_2$), 30.14 (benzyl-<u>CH$_2$</u>), 14.10 (-OCH$_2$<u>CH$_3$</u>).

5-Oxo-3-phenyl-4-phenylamino-4,5-dihydro-[1,2,4]-triazol-5-on-1-yl-acetic acid ethyl ester (8e): Recrystallization from acetone-water (1:2) (yield: 65.18%), mp. 124-126 °C; Analysis (Calc/found %): for $C_{18}H_{18}O_3N_4$ C: 63.89/63.75, H: 5.36/6.32, N: 16.56/16.17; IR (KBr) (ν, cm^{-1}), 3259 (NH), 1787 (ester-C=O), 1702 (triazole-C=O), 1625 (-C=N), 1217 (-C-O); ^{1}H NMR (DMSO-d_6) δ 1.23 (t, -OCH$_2$<u>CH$_3$</u>, J = 7.2 Hz), 4.19 (q, -OCH$_2$, J = 7.2 Hz), 4.76 (s, -NCH$_2$), [ar H: 6.64 (d, 2H, CH-2, CH-6, J =7.8 Hz), 6.85 (t, 1H, CH-4, J = 7.2 Hz), 7.23 (t, 2H, CH-3, CH-5, J = 8.2 Hz), 7.40-7.45 (m, 3H), 7.75-7.90 (m, 2H)], 9.33 (s, -NH); ^{13}C NMR (DMSO-d_6) δ 167.65 (C=O), 152.20 (triazole-C-5), 145.20 (triazole C-3), [ar C: 146.09 (C-1), 130.56 (C-1'), 128.74 (C-3', C-5'), 129.24 (C-3, C-5), 126.73 (C-2', C-6'), 125.70 (C-4'), 120.28 (C-4), 111.99 (C-2, C-6)], 61.25 (-O<u>CH$_2$</u>CH$_3$), 46.50 (-NCH$_2$), 13.92 (-OCH$_2$<u>CH$_3$</u>).

General method for the synthesis of compounds 9

A solution of the corresponding compound **8** (0.01 mol) in *n*-butanol was refluxed with hydrazine hydrate (0.025 mol) for 4 h. After cooling to room temperature, a white solid appeared. This was recrystallized from an appropriate solvent to afford the desired product.

3-Methyl-5-oxo-4-phenylamino-4,5-dihydro-[1,2,4]triazol-1-yl-acetic acid hydrazide (9a): Recrystallization from ethanol (yield: 90.20%), mp. 168-170 °C; Analysis (Calc/found %): for $C_{11}H_{14}O_2N_6$C: 50.38/50.12, H: 5.38/5.31, N: 32.04/31.90; IR (KBr) (ν, cm^{-1}), 3339, 3321,3220 (NH$_2$+ NH), 1715 (triazole-C=O), 1674 (hydrazide-C=O), 1603 (-C=N); ^{1}H NMR (DMSO-d_6) δ 2.09 (s, -CH$_3$), 4.36 (s, -NH$_2$), 4.30(s, -NCH$_2$), [ar H: 6.68 (d, 2H, CH-2, CH-6, J = 7.8 Hz), 6.91 (t, 1H, CH-4, J = 7.4 Hz), 7.25 (t, 2H, CH-3, CH-5, J = 7.6 Hz)], 8.95 (s, -NH, exch. with D$_2$O), 9.34 (s, -<u>NH</u>NH$_2$, exch. with D$_2$O); ^{13}C NMR (DMSO-d_6) δ 165.93 (C=O), 152.31 (triazole C-5), 145.18 (triazole C-3), [ar C: 146.51 (C-1), 129.20 (C-3, C-5), 120.27 (C-4) 112.09 (C-2, C-6)], 38.09 (-NCH$_2$), 10.41 (-CH$_3$).

3-Ethyl-5-oxo-4-phenylamino-4,5-dihydro-[1,2,4]triazol-1-yl-acetic acid hydrazide (9b): Recrystallization from ethanol (yield: 89.60%), mp. 221-223 °C; Analysis (Calc/found %): for $C_{12}H_{16}O_2N_6$C: 52.16/52.25, H: 5.84/5.91, N: 30.42/30.40; IR (KBr) (ν, cm^{-1}), 3311, 3249,3205 (NH$_2$+ NH), 1696 (triazole-C=O), 1680 (hydrazide-C=O),1603 (-C=N); ^{1}H NMR (DMSO-d_6) δ 1.10 (t, -CH$_2$<u>CH$_3$</u>, J = 7.6 Hz), 2.43 (q, -<u>CH$_2$</u>CH$_3$, J = 7.6 Hz), 4.29 (s, -NCH$_2$), 4.33 (s, -NH$_2$), [ar H: 6.65 (d, 2H, CH-2, CH-6, J =7.6 Hz), 6.84 (t, 1H, CH-4, J =7.6 Hz), 7.21 (t, 2H, CH-3, CH-5, J =7.4 Hz)], 8.93 (s, triazole-NH), 9.29 (s, -<u>NH</u>NH$_2$); ^{13}C NMR (DMSO-d_6) δ 165.84 (C=O), 152.37 (triazole C-5), 148.85 (triazole C-3), [ar C: 146.43 (C-1), 129.05 (C-3, C-5), 120.05 (C-4) 111.99 (C-2, C-6)], 46.46 (-NCH$_2$), 17.91 (-<u>CH$_2$</u>CH$_3$), 9.83 (-CH$_3$).

5-Oxo-4-phenylamino-3-n-propyl-4,5-dihydro-[1,2,4]triazol-1-yl-acetic acid hydrazide (9c): Recrystallization from ethanol (yield: 85.40%), mp. 218-220 °C; Analysis (Calc/found %): for $C_{13}H_{18}O_2N_6$ C: 53.78/53.75, H: 6.25/6.27, N: 28.95/29.28; IR (KBr) (ν, cm^{-1}), 3312, 3246,3201 (NH$_2$+ NH), 1697 (triazole-C=O), 1673 (hydrazide-C=O),1604 (-C=N); ^{1}H NMR (DMSO-d_6) δ 0.88 (t, -CH$_2$CH$_2$<u>CH$_3$</u>, J = 7.4 Hz Hz), 1.56 (sex, -CH$_2$<u>CH$_2$</u>CH$_3$, J_1 = 7.0 Hz, J =7.4 Hz), 2.42 (t, -<u>CH$_2$</u>CH$_2$CH$_3$, J = 7.2 Hz), 4.35 (s, -NH$_2$), 4.29 (s, NCH$_2$), [ar H: 6.65 (d, 2H, CH-2, CH-6,J = 7.6 Hz), 6.84 (t, 1H, CH-4, J = 7.4 Hz), 7.22 (t,

2H, CH-3, CH-5, J = 7.6 Hz)], 9.29 (s, -NHNH$_2$) , 8.95 (s,-NH) ; ^{13}C NMR (DMSO-d$_6$) δ 165.89 (C=O), 152.39 (triazole C-5), 147.77 (triazole C-3), [ar C: 146.46 (C-1), 129.08 (C-3, C-5), 120.09 (C-4) 112.02 (C-2, C-6)], 46.47 (-NCH$_2$), 26.15 (-CH$_2$CH$_2$CH$_3$), 18.70 (-CH$_2$CH$_2$CH$_3$), 13.36 (-CH$_2$CH$_2$CH$_3$).

3-Benzyl-5-oxo-4-phenylamino-4,5-dihydro-[1,2,4]triazol-1-yl-acetic acid hydrazide (9d): Recrystallization from ethanol (yield: 68.70%), mp. 208-209 °C; Analysis (Calc/found %): for $C_{17}H_{18}O_2N_6$ C: 60.34/60.45, H: 5.36/5.37, N: 24.84/24.68; IR (KBr) (ν, cm^{-1}), 3340, 3248,3210 (NH$_2$+ NH), 1705 (triazole-C=O), 1669 (hydrazide-C=O), 1603 (-C=N); ^{1}H NMR (DMSO-d$_6$) δ 3.82 (s, benzyl-CH$_2$), 4.31 (s, -NCH$_2$), 4.45 (s, -NH$_2$), [ar H: 6.57 (d, 2H, CH-2, CH-6, J = 7.4 Hz), 6.83 (t, 1H, CH-4, J = 7.4 Hz), 7.15 (t, 2H, CH-3, CH-5, J = 7.8 Hz), 7.20-7.45 (m, 5H)], 9.29 (s, -NHNH$_2$), 8.97 (s, -NH); ^{13}C NMR (DMSO-d$_6$) δ 165.77 (C=O), 152.15 (triazole C-5), 147.00 (triazole C-3), [ar C: 146.31 (C-1), 134.85 (C-1'), 128.83 (C-3', C-5') ,128.25 (C-2', C-6'), 126.80 (C-4'), 126.01 (C-3, C-5), 120.61 (C-4), 112.53 (C-2, C-6)], 46.47 (-NCH$_2$), 30.23 (benzyl-CH$_2$).

5-Oxo-3-phenyl-4-phenylamino-4,5-dihydro-[1,2,4]triazol-1-yl-acetic acid hydrazide (9e): Recrystallization from ethanol (yield: 78.30%), mp. 215-216 °C; Analysis (Calc/found %): for $C_{16}H_{16}O_2N_6$ C: 59.25/59.36, H: 4.97/4.90, N: 25.91/25.58; IR (KBr) (ν, cm^{-1}), 3415, 3325, 3229 (NH$_2$+ NH), 1707 (hydrazide-C=O), 1670 (triazole-C=O), 1614 (-C=N); ^{1}H NMR (DMSO-d$_6$) δ 4.47 (s, 4H, -NCH$_2$+NH$_2$), [ar H: 6.69 (d, 2H, CH-2, CH-6, J = 7.2 Hz), 6.90 (t, 1H, CH-4, J = 7.0 Hz), 7.30 (t, 2H, CH-3, CH-6, J= 7.2 Hz), 7.40-7.70 (m, 3H), 7.80-8.00 (m, 2H)], 9.24 (-NH), 9.40 (s, -NHNH$_2$); ^{13}C NMR (DMSO-d$_6$) δ 165.70 (C=O), 152.50 (triazole C-5), 144.99 (triazole C-3), [ar C: 146.24 (C-1), 130.46 (C-4'), 129.22 (C-3, C-5), 128.71 (C-3', C-5'), 126.73 (C-2', C-6'), 125.67 (C-1'), 120.23 (C-4), 112.16 (C-2, C-6)], 46.88 (-NCH$_2$).

General method for the synthesis of compounds 10

A solution of the corresponding compound **9** (0.01 mol) in ethanol was refluxed with appropriate aldehyde (0.01 mol) for 3 h. After cooling to room temperature, a white solid appeared. This was recrystallized from an appropriate solvent to afford the desired product.

5-Oxo-4-phenylamino-3-n-propyl-4,5-dihydro-[1,2,4]triazol-1-yl-acetic acid p-methoxy-benzylidenehydrazide (10a): Recrystallization from ethanol (yield: 81.13%), mp. 234-237 °C; The ratio of *trans/cis* conformers: 71/29; Analysis (Calc/found %): for $C_{21}H_{24}O_3N_6$ C: 61.75/60.89, H: 5.92/6.12, N: 20.58/21.05; IR (KBr) (ν, cm^{-1}), 3218 (-NH), 3118 (-NHN=), 1716 (triazole-C=O), 1687 (hydrazide-C=O), 1607 (-C=N); ^{1}H NMR (DMSO-d$_6$) δ 0.89 (t, -CH$_2$CH$_2$CH$_3$, J= 7.4 Hz), 1.55 (sex, -CH$_2$CH$_2$CH$_3$, J_1= 7.4 Hz, J_2= 7.2 Hz), 2.42 (t, -CH$_2$CH$_2$CH$_3$, J= 7.2 Hz), 3.80 (s, -OCH$_3$), 4.88 and 4.49 (s, -NCH$_2$, *trans/cis*), [ar H: 6.62 (d, 2H, CH-2, CH-6, J= 8.2 Hz), 6.84 (t, 1H, CH-4, J= 7.2 Hz), 7.21 (t, 2H, CH-3, CH-5, J_1= 7.2 Hz, J_2= 8.2 Hz), 7.67 (d, 2H, CH-2', CH-6', J= 9.0 Hz), 6.99 (d, 2H, CH-3', CH-5', J= 9.0 Hz), 7.96 and 8.14 (s, -N=CH, *trans/cis*), 9.04 (s, -NH), 11.59 and 11.63 (-NHN=, *trans/cis*); ^{13}C NMR (DMSO-d$_6$) δ 167.75 (-C=O), 152.30 (triazole C-5), 148.10(triazole-C-3), 143.80 and 145.05 (-N=CH, *trans/cis*), [ar C: 160.89 (C-4'), 146.49 (C-1), 129.05 (C-3, C-5), 128.47 (C-2', C-6'), 126.39 (C-1'), 120.21 (C-4), 114.15 (C-3', C-5'), 111.95 (C-2, C-6)], 55.62 (-OCH$_3$), 46.40 and 46.80 (-NCH$_2$, *trans/cis*), 26.13 (-CH$_2$CH$_2$CH$_3$), 18.74 (-CH$_2$CH$_2$CH$_3$), 13.30 (-CH$_2$CH$_2$CH$_3$).

5-Oxo-4-phenylamino-3-n-propyl-4,5-dihydro-[1,2,4]triazol-1-yl-acetic acid o-hydroxy- benzylidenehydrazide (10b): Recrystallization from ethyl acetate (yield: 78.94%), mp. 143-144 °C; The ratio

of *trans/cis* conformers: 57/43; Analysis (Calc/found %): for $C_{20}H_{22}O_3N_6$ C: 60.90/61.04, H: 5.62/5.55, N: 21.31/21.22; IR (KBr) (ν, cm^{-1}), 3220 (-NH+OH), 3122 (-NHN=), 1716 (triazole-C=O), 1682 (hydrazide-C=O), 1605 (-C=N); ^{1}H NMR (DMSO-d_6) δ 0.89 (t, -$CH_2CH_2\underline{CH_3}$, J= 7.4 Hz), 1.58 (sex, -$CH_2\underline{CH_2}CH_3$, J_1= 7.4, J_2= 7.2 Hz), 2.42 (t, -$\underline{CH_2}CH_2CH_3$, J= 7.2 Hz), 4.89 and 4.53 (-NCH_2, *trans/cis*), [ar H: 6.62 (d, 2H, CH-2, CH-6, J= 7.2 Hz), 6.80-7.00 (m, 3H, CH-4, CH-3', CH-4'), 7.20-7.40 (m, 3H, CH-3, CH-5, CH-5'), 7.76 and 7.58 (d, 1H, CH-6', J= 7.8 Hz, *trans/cis*], 8.33 and 8.44 (s, -N=CH, *trans/cis*), 9.02 (s, -NH), 10.06 and 10.96 (s, -OH, *trans/cis*), 11.62 and 11.96 (s, -NHN=, *trans/cis*); ^{13}C NMR (DMSO-d_6) δ 167.58 (-C=O), 152.42 and 152.72 (triazole C-5, *trans/cis*), 147.91 and 147.65 (triazole C-3, *trans/cis*), 141.20 and 143.21 (N=CH, *trans/cis*) [ar C: 162.87 and 161.17 (C-2', *trans/cis*), 146.48 (C-1), 131.17 and 131.48 (C-6', *trans/cis*), 129.09 (C-3, C-5), 126.12 (C-5'), 120.11 (C-4), 120.04 (C-4'), 119.30 and 118.54 (C-1', *trans/cis*), 116.24 (C-3'), 111.97 (C-2, C-6)], 46.75 and 46.95 (-NCH_2, *trans/cis*), 26.13 (-$\underline{CH_2}CH_2CH_3$), 18.72 (-$CH_2\underline{CH_2}CH_3$), 13.30 (-$CH_2CH_2\underline{CH_3}$).

5-Oxo-4-phenylamino-3-n-propyl-4,5-dihydro-[1,2,4]triazol-5-on-1-yl-acetic acid 4-hydroxy-3-methoxy-benzylidenehydrazide (10c): Recrystallization from ethanol (yield: 80.53%), mp. 250-252 °C; The ratio of *trans/cis* conformers: 70/30; Analysis (Calc/found %): for $C_{21}H_{24}O_4N_6$ C: 59.42/58.99, H: 5.70/5.82, N: 19.80/20.05; IR (KBr) (ν, cm^{-1}), 3266 (-NH), 3186 (-OH), 3145 (-NHN=), 1705 (triazole-C=O), 1670 (hydrazide-C=O), 1600 (-C=N); ^{1}H NMR (DMSO-d_6) δ 0.88 (t, -$CH_2CH_2\underline{CH_3}$, J= 7.4), 1.57 (sex, -$CH_2\underline{CH_2}CH_3$, J_1= 7.4 Hz, J_2= 7.2 Hz), 2.44 (t, -$\underline{CH_2}CH_2CH_3$, J= 7.2 Hz), 3.81 (s, -OCH_3), 4.89 and 4.48 (-NCH_2, *trans/cis*), [ar H: 6.64-6.68 (m, 2H, CH-2, CH-6), 6.85-6.91 (m, 2H, CH-4, CH-5'), 7.11-7.35 (m, 3H, CH-3, CH-5, CH-6'), 7.36 and 7.27 (s, 1H, CH-2' *trans/cis*,)], 7.89 and 8.01 (s, -N=CH, *trans/cis*), 9.01 (s, -NH), 9.53 and 9.59 (s, -OH, *trans/cis*), 11.52 and 11.54 (s, -NHN=, *trans/cis*); ^{13}C NMR (DMSO-d_6) δ 167.80 (-C=O), 152.85 and 152.03 (triazole C-5, *trans/cis*), 149.15 and 148.91 (triazole C-3, *trans/cis*), 144.58 (-N=CH), [ar C: 162.81 (C-4'), 148.09 (C-3'), 146.69 (C-1), 129.27 (C-3, C-5), 125.46 (C-1'), 121.82 and 122.05 (C-2', *trans/cis*), 120.25 (C-4), 115.43 (C-6'), 112.16 (C-2, C-6), 109.19 (C-5')], 55.60 (-OCH_3), 47.05 and 47.22 (-NCH_2, *trans/cis*), 26.34 (-$\underline{CH_2}CH_2CH_3$), 18.96 (-$CH_2\underline{CH_2}CH_3$), 13.51 (-$CH_2CH_2\underline{CH_3}$).

5-Oxo-4-phenylamino-3-n-propyl-4,5-dihydro-[1,2,4]triazol-1-yl-acetic acid pyridine-4-yl-methylenehydrazide (10d): Recrystallization from ethanol (yield: 83.37%), mp. 216-219 °C; The ratio of *trans/cis* conformers: 70/30; Analysis (% Calc/found): for $C_{19}H_{21}O_2N_7$ C: 60.15/59.63, H: 5.58/5.75, N: 25.84/25.42; IR (KBr) (ν, cm^{-1}), 3238 (-NH), 3118 (-NHN=), 1703 (triazole-C=O), 1685 (hydrazide-C=O), 1608 (-C=N); ^{1}H NMR (DMSO-d_6) δ 0.89 (t, -$CH_2CH_2\underline{CH_3}$, J= 7.4 Hz), 1.57 (sex, -$CH_2\underline{CH_2}CH_3$, J_1= 7.4, J_2= 7.2 Hz), 2.41 (t, -$\underline{CH_2}CH_2CH_3$, J= 7.2 Hz), 4.84 and 4.44 (-NCH_2, *trans/cis*), [ar H: 6.62 (d, 2H, CH-2, CH-6, J= 6.6 Hz), 6.74 (t, 1H, CH-4, J= 6.8 Hz), 6.84 (d, 2H, C-3', C-5', J= 7.6 Hz), 7.21 (t, 2H, CH-3, CH-5, J= 6.8 Hz), 7.52 (d, 2H, CH-2', CH-6', J =7.6 Hz)], 7.88 and 8.05 (s, -N=CH, *trans/cis*), 8.99 (s, -NH), 11.38 and 11.41 (s, -NHN=, *trans/cis*); ^{13}C NMR (DMSO-d_6) δ 167.20 (-C=O), 152.67 and 151.26 (triazole C-5, *trans/cis*), 147.53 triazole C-3), 144.73 (-N=CH), [ar C: 146.44 (C-1), 129.02 (C-3, C-5), 128.10 and 128.34 (C-3', C-5', *trans/cis*), 121.11 (C-4'), 120.01 (C-4), 111.92 (C-2, C-6), 111.61 (C-2',C-6')], 46.65 and 46.82 (-NCH_2, *trans/cis*), 26.09 (-$\underline{CH_2}CH_2CH_3$), 18.69 (-$CH_2\underline{CH_2}CH_3$), 13.26 (-$CH_2CH_2\underline{CH_3}$).

5-Oxo-3-n-propyl-4-phenylamino-4,5-dihydro-[1,2,4]triazol-1-yl-acetic acid thiophene-2-yl-methylenehydrazide (10e): Recrystallization from ethanol-ethyl acetate (1:1) (yield: 72.77%), mp.200-202 °C; The ratio of *trans/cis* conformers: 62/38; Analysis (Calc/found %): for $C_{18}H_{20}O_2N_6S$ C: 56.23/56.43,

H: 5.24/5.15, N: 21.86/21.42; IR (KBr) (ν, cm^{-1}), 3221 (-NH), 3115 (-NHN=), 1717 (triazole-C=O), 1685 (hydrazide-C=O), 1602 (-C=N); ^{1}H NMR (DMSO-d_6) δ 0.89 (t, -$CH_2CH_2\underline{CH_3}$, J= 7.4), 1.57 (sex, -$CH_2\underline{CH_2}CH_3$, J_1= 7.4, J_2= 7.2), 2.41 (t, -$\underline{CH_2}CH_2CH_3$, J= 7.2), 4.81 and 4.48 (s, -NCH_2, *trans/cis*), [ar H: 6.61 (d, 2H, CH-2, CH-6, J= 7.8 Hz), 6.84 (t, 1H, CH-4, J= 7.4 Hz), 7.11-7.27 (m, 3H, CH-3, CH-5, C-5'), 7.45 (t, 1H, C-4' J= 4.4 Hz), 7.66 (d, 1H, C-3' J= 4.4 Hz)], 8.20 and 8.42 (s, -N=CH, *trans/cis*), 9.02 (s, -NH), 11.69 and 11.71 (s, -NHN=, *trans/cis*), ^{13}C NMR (DMSO-d_6) δ 167.49 (-C=O), 152.71 and 152.50 (triazole C-5, *trans/cis*), 147.92 and 147.75 (triazole C-3, *trans/cis*), 142.48 and 139.24 (-N=CH, *trans/cis*), [ar C: 146.46 (C-1), 138.61 (C-2'), 130.65 (C-5'), 129.10 (C-3, C-5), 129.06 (C-3'), 127.83 (C-4'), 120.12 (C-4), 111.98 (C-2, C-6)], 46.43 and 47.04 (-NCH_2, *trans/cis*), 26.13 (-$\underline{CH_2}CH_2CH_3$), 18.74 (-$CH_2\underline{CH_2}$ CH_3), 13.29 (-$CH_2CH_2\underline{CH_3}$).

General method for the synthesis of compounds 11

Corresponding compound **10** (0.01 mol) was heated with an equivalent amount of benzoic acid (or acetic acid) at 130-140 °C for 2 h in an oil bath. After cooling to room temperature, a solid appeared. This crude product was recrystallized from DMSO-water (1:2) to afford the desired compound.

3,6-Di(3-methyl-5-Oxo-4-phenylamino-4,5-dihydro-[1,2,4]triazol-1-yl)methyl-1,4-dihydro-[1,2,4,5]tetrazine (11a): (yield: 82.45%), mp. 286 °C; Analysis (Calc/found %): for $C_{22}H_{24}O_2N_{12}$ C: 54.09/54.83, H: 4.95/4.92, N: 34.41/34.44; IR (KBr) (ν, cm^{-1}), 3289 (-NH), 3132 (-NH), 1692 (-C=O), 1644 (-C=N), 1605 (-C=N); ^{1}H NMR (DMSO-d_6) δ 0.87 (s, -$2CH_3$), 4.43 (s, -$2NCH_2$), [ar H: 6.88 (bs, 4H, 2CH-2, 2CH-6), 7.19 (bs, 2H, 2CH-4), 7.56 (d, 4H, 2CH-3, 2CH-5 J = 7.2 Hz)], 8.97 (triazole-2NH), 10.35 (tetrazine-2NH); ^{13}C NMR (DMSO-d_6) δ 163.57 (tetrazine 2C-3, 2C-6), 152.39 (triazole 2C-5), 148.09 (triazole 2C-3), [ar C: 146.35 (2C-1), 128.10 (2CH-3, 2CH-5), 121.01 (2CH-4), 111.78 (2CH-2, 2CH-6)], 45.97 ($2NCH_2$), 13.46 ($2CH_3$).

3,6-Di(3-ethyl-5-Oxo-4-phenylamino-4,5-dihydro-[1,2,4]triazol-1-yl)methyl-1,4-dihydro-o[1,2,4,5]tetrazine (11b): (yield: 83.67%), mp. 274 °C; Analysis (Calc/found %): for $C_{24}H_{28}O_2N_{12}$ C: 55.80/55.89, H: 5.46/5.90, N: 32.54/31.67; IR (KBr) (ν, cm^{-1}), 3288 (-NH), 3132 (-NH), 1697 (-C=O), 1640 (-C=N), 1607 (-C=N); ^{1}H NMR (DMSO-d_6) δ 1.20 (t, -$2CH_2\underline{CH_3}$, J = 7.4 Hz), 2.42 (q, $2\underline{CH_2}CH_3$, J = 7.4 Hz), 4.42 (s, $2NCH_2$), [ar H: 6.83 (bs, 4H, 2CH-2, 2CH-6)), 7.24 (bs, 2H, 2CH-4), 7.44 (bs, 4H, 2CH-3, 2CH-5)], 8.97 (triazole-2NH), 10.34 (tetrazine-2NH); ^{13}C NMR (DMSO-d_6) δ 163.28 (tetrazine 2C-3, 2C-6), 152.39 (triazole 2C-5), 148.08 (triazole 2C-3), [ar C: 146.37 (2C-1), 128.31 (2CH-3, 2CH-5), 120.92 (2CH-4), 112.03 (2CH-2, 2CH-6)], 45.90 ($2NCH_2$), 26.07 ($2\underline{CH_2}CH_3$), 13.44 ($2CH_2\underline{CH_3}$).

3,6-Di(5-Oxo-3-n-propyl-4-phenylamino-4,5-dihydro-[1,2,4]triazol-1-yl)methyl-1,4-dihydro-[1,2,4,5]tetrazine (11c): (yield: 80.98%), mp. 267 °C; Analysis (Calc/found %): for $C_{26}H_{32}O_2N_{12}$ C: 57.34/57.89, H: 5.92/5.90, N: 30.86/30.67; IR (KBr) (ν, cm^{-1}), 3288 (-NH), 3130 (-NH), 1698 (-C=O), 1643 (-C=N), 1604 (-C=N); ^{1}H NMR (DMSO-d_6) δ 0.84 (t, $2CH_2CH_2\underline{CH_3}$, J = 7.4 Hz), 1.53 (m, $2CH_2\underline{CH_2}CH_3$), 2.39 (t, $2\underline{CH_2}CH_2CH_3$,$J$ = 7.4 Hz), 4.42 (s, $2NCH_2$), [ar H: 6.83 (d, 4H, 2CH-2, 2CH-6,J = 7.6 Hz), 7.21 (t, 2H, 2CH-4, J = 7.4 Hz), 7.59 (t, 4H, 2CH-3, 2CH-5, J = 7.6 Hz)], 8.97 (triazole-2NH), 10.35 (tetrazine-2NH); ^{13}C NMR (DMSO-d_6) δ 165.12 (tetrazine -2C-3, 2C-6), 152.37 (triazole 2C-5), 147.85 (triazole 2C-3), [ar C: 146.38 (2C-1), 129.03 (2CH-3, 2CH-5), 120.03 (2CH-4), 111.92 (2CH-2, 2CH-6)], 46.17 ($2NCH_2$),

26.07 ($2\underline{CH_2}CH_2CH_3$), 18.63 ($2CH_2\underline{CH_2}CH_3$), 13.29 ($2CH_2CH_2\underline{CH_3}$).

3,6-Di(3-benzyl-5-Oxo-4-phenylamino-4,5-dihydro-[1,2,4]triazol-1-yl)methyl-1,4-dihydro-[1,2,4,5]tetrazine (11d): (yield: 82.28%), mp. 252 °C; Analysis (Calc/found %): for $C_{34}H_{32}O_2N_{12}$ C: 63.74/63.59, H: 5.03/5.07, N: 26.23/26.45; IR (KBr) (ν, cm^{-1}), 3288 (-2NH), 3136 (-2NH), 1699 (-C=O), 1643 (-C=N), 1604 (-C=N); ^{1}H NMR (DMSO-d_6) δ 3.80 (s, $2CH_2$), 4.32 (s, $2NCH_2$), [ar H: 6.58 (d, 4H, 2CH-2, 2CH-6 J = 7.4 Hz), 6.83 (t, 2H, 2CH-4, J = 7.4 Hz), 7.13 (t, 4H,CH-3, CH-5, J = 7.8 Hz), 7.25-7.42 (m, 10H, benzyl-CH)], 8.95 (triazole-2NH), 10.33 (tetrazine-2NH); ^{13}C NMR (DMSO-d_6) δ 165.21 (tetrazine 2C-3, 2C-6), 152.87 (triazole 2C-5), 147.01 (triazole 2C-3), [ar C: 146.30 (2C-1), 134.12 (2C-1'), 131.39 (2C-3', 2C-5'), 129.22 (2C-2', 2C-6'), 126.61 (2C-4'), 124.62 (2C-3, 2C-5), 119.27 (2C-4), , 112.15 (2CH-2, 2CH-6)], 46.47 ($2NCH_2$), 30.20 ($2CH_2$).

3,6-Di(5-Oxo-3-phenyl-4-phenylamino-4,5-dihydro-[1,2,4]triazol-5-on-1-yl)methyl-1,4-dihydro −[1,2,4,5]tetrazine (11e): (yield: 85.25%), mp. 292 °C; Analysis (Calc/found %): for $C_{32}H_{28}O_2N_{12}$ C: 62.74/63.19, H: 4.61/4.67, N: 27.43/27.15; IR (KBr) (ν, cm^{-1}), 3288 (-NH), 3135 (-NH), 1694 (-C=O), 1640 (-C=N), 1602 (-C=N); ^{1}H NMR (DMSO-d_6) δ 4.45 (s, $2NCH_2$), [ar H: 6.71 (d, 4H, 2CH-2, 2CH-6, J = 7.2), 6.91 (t, 2H,2CH-4, J = 7.4 Hz), 7.30 (t, 4H, 2CH-3, 2CH-5, J = 7.2 Hz), 7.43-7.72 (m, 6H), 7.80-8.03 (m, 4H)], 9.25 (triazole-2NH), 10.35 (tetrazine-2NH); ^{13}C NMR (DMSO-d_6) δ 164.92 (tetrazine-2C-3, 2C-6), 152.50 (triazole-2C-5), 147.92 (triazole 2C-3), [ar C: 146.93 (2C-1), 135.91 (2C-4'), 132.46 (2C-3, 2C-5), 130.45 (2C-3', 2C-5'), 127.31 (2C-2', 2C-6'), 125.56 (2C-1'), 119.34 (2C-4), 114.85 (2CH-2, 2C-6)], 46.87 ($2NCH_2$).

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