The Islamic University Journal (Series of Natural Studies and Engineering)
Vol.14, No.2, P.11-20, 2006, ISSN 1726-6807, http//www.iugaza.edu.ps/ara/research/

SYNTHESIS OF SOME NEW DERIVATIVES OF 1,3,4,5-TETRASUBSTITUTED-1H-1,2,4-TRIAZOLES BY REACTION OF NITRILIMINES WITH ALDEHYDE METHOXYCARBONYIHYDRAZONES

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ملخص: تتفاعل أمينات النيترايل **(2)** مع ميثوكسي كاربونيل هيدرازونات الألدهيدات **(3-5)** لتعطي مركبات 3-أسيتيل-5-ألكيل-1-أريل-5,4- ثنائي هيدرو-4-(ميثوكسي كاربونيل أمينو)- 4,2,1 -ترايازولات **(6-8)**. وقد تم تحديد بنى هذه المركبات من خلال دراسة أطيافها المختلفة مثل طيف الأشعة تحت الحمراء وطيف الكتلة وأطياف الرنين النووي المغناطيسي.

ABSTRACT: Nitrilimines (**2a-e**) react with aldehyde methoxycarbonylhydrazones (**3-5**) to afford 3-acetyl-5-alkyl-1-aryl-4-(methoxycarbonylamino)-4,5-dihydro-1H-1,2,4-triazoles (**6-8a-e**). The structure of these compounds was elucidated by IR, MS and NMR spectral data.

Key Words: Hydrazonoyl chlorides; Nitrilimines; 1,2,4-Triazoles; Aldehyde methoxycarbonylhydrazones.

Introduction

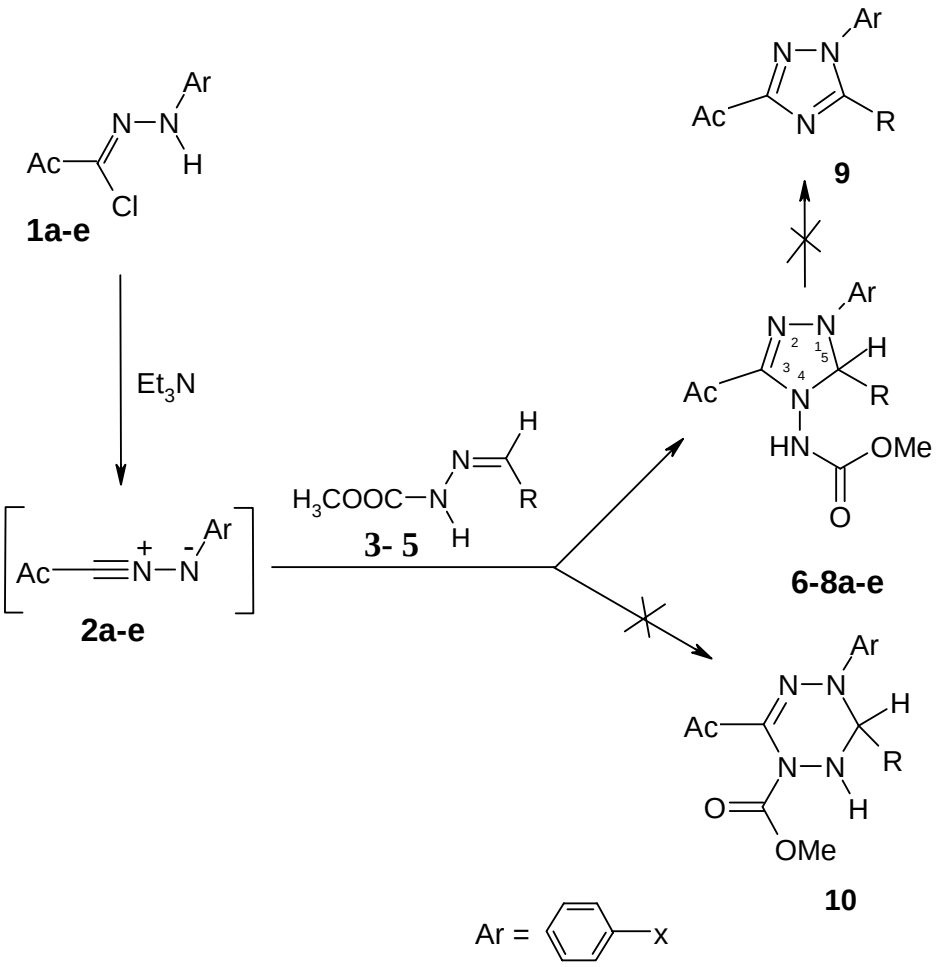
Substituted 1,2,4-triazoles have several significant applications. They are used as dyes, biological reagents, photographic chemicals, precursors for the synthesis of peptidomimetics, and in synthesis of polymers [1]. The highly reactive nitrilimines **(2)** are potent intermediates in heterocyclic synthesis by 1,3-dipolar cycloaddition reactions, especially, with dipolarophiles containing (C=N) to yield 1,2,4-triazoles [2].

Recently, the synthesis of substituted 4,5-dihydro-1,2,4-triazoles from nitrilimines and different ketoximes was reported [3-5]. On the other hand, the reaction of acetaldoxime with nitrilimines yields directly the aromatic

1,2,4-triazole via loss of water [6]. Nitrilimines react with hydrazones in different modes depending on their substitutions: the reaction with aliphatic ketohydrazones carrying electron withdrawing groups yields 1,2,4-triazoles via cycloaddition reaction [7,8]; on the other hand, methyl hydrazones of aliphatic ketones give cyclocondensation 1,2,4,5-tetrazine products rather than the cycloaddition triazole products [9,10]. Simple hydrazones afford initially the acyclic electrophilic addition products, which cyclize to 1,2,4,5-tetrazines upon treatment with Pd-C at room temperature [11]. Accordingly, we investigated the reaction of aldehyde methoxycarbonylhydrazones **(3-5)** with nitrilimines **(2).** This reaction can undergo cycloaddition on the C=N double bond affording the dihydro-1,2,4-triazoles. The later can eliminate methyl carbamate giving the aromatic 1,2,4-trizole. Another possible mode is the cycolcondensation reaction leading to 1,2,4,5-tetrazines.

Results and Discussion

The aldehyde methoxycarbonylhydrazones **(3-5)** were prepared through the reaction of methyl carbazates (H_2NNHCO_2Me) with acetaldehyde, propionaldehyde and cyclohexanecarbaldehyde in methanol [12]. Nitrilimines **2,** were prepared *in situ* from the respective hydrazonoyl chlorides **1** by reaction with triethylamine [13,14], and immediately coupled with aldehyde methoxycarbonylhydrazones **(3-5)** at room temperature affording the corresponding 1,2,4-triazoles (**6-8a-e)** with yields of (60-80%) scheme 1. The structure of these products was established by IR, MS, and NMR spectral data.



No.	3/6	4/7	5/8
R	CH_3	CH_3CH_2	

	a	b	c	d	e
x	Cl	Br	H	CH_3	F

Scheme 1

The EI-MS spectra of compounds **6-8** display the correct molecular ions based on their formulae. This excludes formation of the aromatic 1,2,4-triazoles **(9)**. The base peak of these compounds **6-8** is that of $M^{+\cdot}$ - CH_3, $M^{+\cdot}$- CH_2CH_3 and $M^{+\cdot}$ - C_6H_{11}, respectively, Other important fragments are (CH_3CO^+), (Ar^+) and (CH_3COO^+).

The IR spectra of compounds **6-8** revealed a strong absorption band in the region 3322-3200 cm^{-1} (N-H). Two strong absorption bands are also observed in the region 1680-1670 cm^{-1} ($CH_3C=O$) and 1730-1710 cm^{-1} ($CH_3OC=O$). The (C=N) stretching band appears in the region 1620-1600 cm^{-1}.

The ^{1}H-NMR spectra of compounds **6** show a singlet for the $CH_3C=O$ around 2.5 ppm, a singlet for the OCH_3 around 3.7 ppm, a doublet for the methyl group on C-5 at 1.6 ppm and a quartet for C5-H about 5.5 ppm. The signals of the aromatic protons and NH appear between 7.7-7.0 ppm. Compounds **7** show a triplet for the ($CH_2\mathbf{CH_3}$) around 1.0 ppm and a multiplet for the ($\mathbf{CH_2}CH_3$) at 1.9 ppm. The C5-H proton appears as a triplet at about 5.4 ppm. Compounds **8** show a multiplet for the cyclohexyl group on C-5 in the region 2.0-1.1 ppm. The C5-H proton appears as a doublet around 5.4 ppm.

The C_5-H protons of compounds **6-8** appear about 5.5 ppm as a quartet, triplet and multiplet, respectively. However, compounds **10**, if they were formed, will exhibit C_5-H as a multiplet due to coupling of this proton with the NH and with the methyl, ethyl and cyclohexyl groups, respectively. The NH of the six-membered ring structure is expected to appear at 4-5 ppm [8,9] which excludes the formation of compounds **10**.

The ^{13}C-NMR spectra display the characteristic signals of the suggested structures **(6-8).** The signals for C-5 appear at 80.3 ppm but in the case of the six membered heterocyclic structures **10** it is expected to appear a C-6 signal at about 70.0 ppm [8].

Thus, the obtained products confirm the cycloaddition reaction without any elimination of methyl carbazate to get the aromatic 1,2,4-triazole **(9)**, but not the cyclocondensation reaction leading to six membered tetrazine rings **10**.

Experimental

Methyl carbazate, cyclohexane carbaldehyde and propionaldehyde were purchased from Acros. Melting points were determined on an electrothermal Mel-Temp. apparatus and are uncorrected. IR spectra were obtained by using Perkin-Elmer 237 infrared spectrometer in KBr discs. Electron impact mass spectra were run on Finnigan MAT 8200 and 8400 spectrometers at 70 eV. ^{1}H and ^{13}C-NMR were recorded on a Bruker AM 300 MHz NMR spectrometer using $CDCl_3$ as a solvent at 21°C and TMS as an internal reference. Chemical shifts are expressed in δ(ppm) downfield from TMS and coupling constants are in Hertz (Hz). Elemental analysis were performed at Cairo University, Egypt.

Hydrazonoyl chlorides **(1a-e)** were prepared via direct coupling of the appropriate arenediazonium chloride with 3-chloro-2,4-pentanedione in aqueous pyridine solution following standard procedures [13,14].
The aldehyde methoxycarbonylhydrazones **(3-5)** were prepared through the reaction of methyl carbazates (H_2NNHCO_2Me) with different aldehydes in absolute methanol, the reaction mixture was refluxed for 2-3 hours, and then stirring was continued overnight following standard procedures [12].

Synthesis of 1,2,4-triazoles (6-8a-e)
Triethylamine (0.05 mol) was dropwise added to a stirred solution of hydrazonoyl chlorides (0.01 mol) and aldehyde carbomethoxyhydrazone (0.015 mol) in THF (60 ml) at room temperature. Stirring of the reaction mixture was continued at room temperature for 24-48 hours. The organic solvent was then removed in vacuum, and the residue was washed with water (4 x 100 ml). The residual crude solid product was then crystallized from ethanol. Some compounds were further purified on preparative TLC plates, using silica gel as an adsorbent and $CHCl_3$/EtOH (95:5 v/v) as the developing solvent. The following compounds were prepared by this method:

3-Acetyl-1-(4-chlorophenyl)-4-(methoxycarbonylamino)-5-methyl-4,5-dihydro-1H-1,2,4-triazole (6a).
Yield=54%, m.p = 175-177 °C**,** ^{1}H NMR ($CDCl_3$): 1.6 (d, 3H, CH_3), 2.5 (s, 3H, CH_3CO), 3.7 (s, 3H, OCH_3), 5.4 (q, 1H, C5-H), 7.7 - 7.0 (m, 5H, 1NH + 4H for aromatic protons underneath); ^{13}C NMR ($CDCl_3$): 20.3 (CH_3), 26.1 (**CH_3**CO), 53.0 (O**CH_3**), 81.0 (C-5), 141.3, 130.7, 129.2, 115.5 (aromatic carbons), 145.4 (C=N), 156.5 (CH_3O**C=O**), 189.2 (CH_3**C=O**). IR: cm^{-1} = 3219 (NH), 1719 (OC=O), 1679 (C=O acetyl). MS: *m/z* ($C_{13}H_{15}ClN_4O_3$) = 310 ($M^{+\cdot}$), 295 (base beak, $M^{+\cdot}$-CH_3), 111 ($C_6H_4Cl^+$), 59 ($MeCOO^+$), 43 ($MeCO^+$). Elemental analysis: calcd.(%): C 50.25, H 4.48, N 18.03, found (%): C 50.40, H 4.18, N 18.01.

3-Acetyl-1-(4-bromophenyl)-4-(methoxycarbonylamino)-5-methyl-4,5-dihydro-1H-1,2,4-triazole (6b).
Yield = 50%, m.p = 180-182 °C, ^{1}H NMR ($CDCl_3$): 1.6 (d, 3H, CH_3), 2.5 (s, 3H, CH_3CO), 3.7 (s, 3H, OCH_3), 5.4 (q, 1H, C5-H), 7.4 - 7.0 (m, 5H, 1NH +

4H for aromatic protons underneath); ^{13}C NMR ($CDCl_3$): 20.3 (CH_3), 26.2 (**CH_3** CO), 53.0 (O**CH_3**), 80.6 (C-5), 141.7, 133.7, 132.8, 114.2 (aromatic carbons), 145.2 (C=N), 156.5 (CH_3O**C=O**), 189.2 (CH_3**C=O**). IR: cm $^{-1}$ = 3227 (NH), 1716 (OC=O), 1674 (C=O acetyl). MS: *m/z* ($C_{13}H_{15}BrN_4O_3$) = 354 ($M^{+\cdot}$), 339 (base beak, $M^{+\cdot}$-CH_3), 155 ($C_6H_4Br^+$), 59 ($MeCOO^+$), 43 ($MeCO^+$). Elemental analysis: calcd.(%): C 43.96, H 4.26, N 15.77, found(%): C 44.15, found(%): C 44.15, H 4.50, N 15.60.

3-Acetyl-4-(methoxycarbonylamino)-5-methyl-1-phenyl-4,5-dihydro-1H-1,2,4-triazole (6c).

Yield = 52%, m.p = 128-130 $^{\circ}$C, ^{1}H NMR ($CDCl_3$): 1.6 (d, 3H, CH_3), 2.5 (s, 3H, CH_3CO), 3.7 (s, 3H, OCH_3), 5.5 (q, 1H, C5-H), 7.4 - 7.0 (m, 5H, 1NH + 4H for aromatic protons underneath); ^{13}C NMR ($CDCl_3$): 20.4 (CH_3), 26.1 (**CH_3**CO), 52.9 (O**CH_3**), 80.4 (C-5), 142.2, 130.4, 129.2, 114.4 (aromatic carbons), 145.4 (C=N), 156.6 (CH_3O**C=O**), 189.3 (CH_3**C=O**). IR: cm $^{-1}$ = 3260 (NH), 1724 (OC=O), 1686 (C=O acetyl). MS: *m/z* ($C_{13}H_{16}N_4O_3$) = 276 ($M^{+\cdot}$), 261 (base beak, $M^{+\cdot}$-CH_3), 77 ($C_6H_5^+$), 59 ($MeCOO^+$), 43 ($MeCO^+$).

3-Acetyl-4-(methoxycarbonylamino)-5-methyl-1-(4-methylphenyl)-4,5-dihydro-1H-1,2,4-triazole (6d).

Yield = 67%, m.p = 156-158 $^{\circ}$C, ^{1}H NMR ($CDCl_3$): 1.6 (d, 3H, CH_3), 2.3 (s, 3H, CH_3CO), 2.4 (s, 3H, Ar**CH_3**), 3.7 (s, 3H, OCH_3), 5.4 (q, 1H, C_5-H), 7.2-7.0 (m, 5H, 1NH + 4H for aromatic protons underneath); ^{13}C NMR ($CDCl_3$): 20.3 (CH_3), 20.7 (Ar**CH_3**), 26.0 (**CH_3**CO), 52.8 (O**CH_3**), 81.0 (C-5), 140.4, 131.9, 130.2, 114.8 (aromatic carbons), 145.1 (C=N), 156.6 (CH_3O**C=O**), 189.2 (CH_3**C=O**). IR: cm^{-1} = 3219 (NH), 1720 (OC=O), 1680 (C=O acetyl). MS: *m/z* ($C_{14}H_{18}N_4O_3$) = 290 ($M^{+\cdot}$), 275 (base beak, $M^{+\cdot}$-CH_3), 91 ($C_7H_7^+$), 59 ($MeCOO^+$), 43 ($MeCO^+$).

3-Acetyl-1-(4-fluorophenyl)-4-(methoxycarbonylamino)-5-methyl-4,5-dihydro-1H-1,2,4-triazole (6e).

Yield = 48%, m.p = 153-154 $^{\circ}$C, IR: cm $^{-1}$ = 3230 (NH), 1716 (OC=O), 1675 (C=O acetyl). MS: *m/z* ($C_{13}H_{15}N_4O_3$) = 294 ($M^{+\cdot}$), 279 (base beak, $M^{+\cdot}$-CH_3), 95 ($C_6H_4F^+$), 59 ($MeCOO^+$), 43 ($MeCO^+$).

3-Acetyl-1-(4-chlorophenyl)-5-ethyl-4-(methoxycarbonylamino)-4,5-dihydro-1H-1,2,4-triazole (7a).
Yield = 40%, m.p = 146-147 °C, ^{1}H NMR ($CDCl_3$): 2.5 (s, 3H, CH_3CO), 1.0 (t, 3H, $CH_2\mathbf{CH_3}$), 2.0 (m, 2H, $\mathbf{CH_2}CH_3$), 3.7 (s, 3H, OCH_3), 5.4 (t, 1H, C5-H), 7.3 - 7.1 (m, 5H, 1NH + 4H for aromatic protons underneath); ^{13}C NMR ($CDCl_3$): 6.6 ($CH_2\mathbf{CH_3}$), 26.1 ($\mathbf{CH_3}CO$), 29.7 ($\mathbf{CH_2}CH_3$), 52.9 ($O\mathbf{CH_3}$), 84.1 (C-5), 141.2, 129.2, 126.7, 115.3 (aromatic carbons) 145.6 (C=N), 156.4 ($CH_3O\mathbf{C=O}$), 189.2 ($CH_3\mathbf{C=O}$). IR: cm^{-1} = 3309 (NH), 1715 (OC=O), 1679 (C=O acetyl). MS: *m/z* ($C_{14}H_{17}ClN_4O_3$) = 324 ($M^{+\cdot}$), 295 (base beak, $M^{+\cdot}$-CH_3CH_2), 111 ($C_6H_4Cl^+$), 59 ($MeCOO^+$), 43 ($MeCO^+$).

3-Acetyl-1-(4-bromophenyl)-5-ethyl-4-(methoxycarbonylamino)-4,5-dihydro-1H-1,2,4-triazole (7b).
Yield = 27%, M.P = 149-150 °C, IR: cm^{-1} = 3302 (NH), 1710 (OC=O), 1675 (C=O acetyl). MS: *m/z* ($C_{14}H_{17}BrN_4O_3$) = 367 ($M^{+\cdot}$), 338 (base beak, $M^{+\cdot}$-CH_3CH_2), 155 ($C_6H_4Br^+$), 59 ($MeCOO^+$), 43 ($MeCO^+$).

3-Acetyl-5-ethyl-4-(methoxycarbonylamino)-1-phenyl-4,5-dihydro-1H-1,2,4-triazole(7c).
Yield = 38%, m.p = 144-145 °C, ^{1}H NMR ($CDCl_3$): 2.5 (s, 3H, CH_3CO), 1.0 (t, 3H, $CH_2\mathbf{CH_3}$), 1.9 (m, 2H, $\mathbf{CH_2}CH_3$), 3.7 (s, 3H, OCH_3), 5.5 (t, 1H, C5-H), 7.3 - 7.1 (m, 6H, 1NH + 5H for aromatic protons underneath); ^{13}C NMR ($CDCl_3$): 6.6 ($CH_2\mathbf{CH_3}$), 26.1 ($\mathbf{CH_3}CO$), 26.2 ($\mathbf{CH_2}CH_3$), 52.8 ($O\mathbf{CH_3}$), 84.7 (C- 5), 142.6, 129.3, 121.8, 114.2 (aromatic carbons), 145.4 (C=N), 156.5 ($CH_3O\mathbf{C=O}$), 189.1 ($CH_3\mathbf{C=O}$). IR: cm^{-1} = 3322 (NH), 1706 (OC=O), 1683 (C=O acetyl). MS: *m/z* ($C_{14}H_{18}N_4O_3$) = 290 ($M^{+\cdot}$), 261 (base beak, $M^{+\cdot}$-CH_3CH_2), 77 ($C_6H_5^+$), 59 ($MeCOO^+$), 43 ($MeCO^+$).

3-Acetyl-5-ethyl-1-(4-methylphenyl)-4-(methoxycarbonylamino)-4,5-dihydro-1H-1,2,4-triazole (7d).
Yield = 37%, m.p = 139-140 °C, ^{1}H NMR ($CDCl_3$): 0.9 (t, 3H,$CH_2\mathbf{CH_3}$), 1.9 (m, 2H, $\mathbf{CH_2}CH_3$), 2.3 (s, 3H, $Ar\mathbf{CH_3}$), 2.5 (s, 3H, CH_3CO), 3.7 (s, 3H, OCH_3), 5.4 (t, 1H, C5-H), 7.4 - 7.1 (m, 5H, 1NH + 4H for aromatic protons underneath); ^{13}C NMR ($CDCl_3$): 6.6 ($CH_2\mathbf{CH_3}$), 20.6 ($Ar\mathbf{CH_3}$), 26.0 ($\mathbf{CH_3}CO$), 26.1 ($\mathbf{CH_2}CH_3$), 52.7 ($O\mathbf{CH_3}$), 84.0 (C-5), 140.3, 131.4, 129.7, 114.5 (aromatic carbons), 145.2 (C=N), 156.5 ($CH_3O\mathbf{C=O}$), 189.0 ($CH_3\mathbf{C=O}$); IR: cm^{-1} = 3225 (NH), 1707 (OC=O), 1679 (C=O acetyl). MS: *m/z* ($C_{15}H_{20}N_4O_3$) = 304 ($M^{+\cdot}$), 275 (base beak, $M^{+\cdot}$-CH_3CH_2), 91 ($C_7H_6^+$), 59 ($MeCOO^+$), 43 ($MeCO^+$).

3-Acetyl-5-ethyl-1-(4-fluorophenyl)-4-(methoxycarbonylamino)-4,5-dihydro-1H-1,2,4-triazole (7e).

Yield = 39%, m.p = 147-148 °C, ^{1}H NMR ($CDCl_3$): 2.5 (s, 3H, CH_3CO), 0.9 (t, 3H, $CH_2\mathbf{CH_3}$), 1.9 (m, 2H, $\mathbf{CH_2}CH_3$), 3.7 (s, 3H, OCH_3), 5.4 (t, 1H, C5-H), 7.3 -7.0 (m, 5H, 1NH + 4H for aromatic protons underneath); ^{13}C NMR ($CDCl_3$): 6.6 ($CH_2\mathbf{CH_3}$), 26.1 ($\mathbf{CH_3}CO$), 26.6 ($\mathbf{CH_2}CH_3$), 52.8 ($O\mathbf{CH_3}$), 84.3 (C-5), 139.4, 131.1, 129.6, 115.8 (aromatic carbons), 145.6 (C=N), 156.8 ($CH_3O\mathbf{C=O}$), 189.1 ($CH_3\mathbf{C=O}$); IR: cm $^{-1}$ = 3237 (NH), 1674 (C=O acetyl), 1721 (OC=O). MS: *m/z* ($C_{14}H_{17}FN_4O_3$) = 308 ($M^{+\cdot}$), 279 (base beak, $M^{+\cdot}$-CH_3CH_2), 95 ($C_6H_4F^+$), 59 ($MeCOO^+$), 43 ($MeCO^+$).

3-Acetyl-1-(4-bromophenyl)-5-cyclohexyl-4-(methoxycarbonylamino)-4,5-dihydro-1H-1,2,4-triazole (8b).

Yield = 22%, m.p = 118-120 °C, ^{1}H NMR ($CDCl_3$): 2.5 (s, 3H, CH_3CO), 2.0-1.2 (m, 11H, cyclohexyl), 3.6 (s, 3H, OCH_3), 5.4 (d, 1H, CH), 7.3 - 7.0 (m, 5H, 1NH + 4H for aromatic protons underneath); ^{13}C NMR ($CDCl_3$): 25.3 ($\mathbf{CH_3}CO$), 40.3-24.2 (cyclohexane carbons), 52.9 ($O\mathbf{CH_3}$), 87.5 (C-5), 142.5, 131.2, 129.8, 116.1 (aromatic carbons), 147.9 (C=N),. 156.2 ($CH_3O\mathbf{C=O}$), 189.3 ($CH_3\mathbf{C=O}$); IR: cm $^{-1}$ = 3310 (NH), 1714 (OC=O), 1680 (C=O acetyl).

3-Acetyl-5-cyclohexyl-4-(methoxycarbonylamino)-1-phenyl-4,5-dihydro -1H-1,2,4-triazole (8c).

Yield = 23%, m.p = 138-140 °C, ^{1}H NMR ($CDCl_3$): 2.5 (s, 3H, CH_3CO), 2.0-1.2 (m, 11H, cyclohexyl), 3.6 (s, 3H, OCH_3), 5.4 (d, 1H, CH), 7.3-7.0 (m, 6H, 1NH + 5H for aromatic protons underneath); ^{13}C NMR ($CDCl_3$): 26.1 ($\mathbf{CH_3}CO$), 40.9-24.2 (cyclohexane carbons), 52.7 ($O\mathbf{CH_3}$), 87.6 (C-5), 142.4, 129.2, 121.3, 114.3 (aromatic carbons), 145.74 (C=N), 156.3 ($CH_3O\mathbf{C=O}$), 188.7 ($CH_3\mathbf{C=O}$), . IR: cm $^{-1}$ = 3309 (NH), 1720 (OC=O), 1683 (C=O acetyl). MS: *m/z* ($C_{18}H_{24}N_4O_3$) = 344 ($M^{+\cdot}$), 261 (base beak, $M^{+\cdot}$-C_6H_{11}), 77 ($C_6H_5^+$), 59 ($MeCOO^+$), 43 ($MeCO^+$).

3-Acetyl-5-cyclohexyl-4,5-dihydro-4-(methoxycarbonylamino)-1-(4-methylphenyl)-1H-1,2,4-triazole (8d).
Yield = 20%, M.P = 105-107 °C, ^{1}H NMR ($CDCl_3$): 1.8-1.1 (m, 11H, cyclohexane hydrogens), 1.9 (s, 3H, $ArCH_3$), 2.5 (s, 3H, CH_3CO), 3.7 (s, 3H, OCH_3), 5.3 (d, 1H, C5-H), 7.4-7.0 (m, 5H, 1NH + 4H for aromatic protons underneath); ^{13}C NMR ($CDCl_3$): 20.7 ($ArCH_3$), 26.1 (CH_3CO), 40.9 - 24.2 (cyclohexane carbons), 52.8 (OCH_3), 87.4 (C-5), 141.6, 132.1, 115.7, 113.9 (aromatic carbons), 145.7 (C=N), 156.3 ($CH_3OC=O$), 189.1 ($CH_3C=O$); IR: cm^{-1} = 3306 (NH), 1717 (OC=O), 1680 (C=O acetyl).

3-Acetyl-5-cyclohexyl-1-(4-fluorophenyl)-4-(methoxycarbonylamino)-4,5-dihydro-1H-1,2,4-triazole (8e).
Yield = 20%, M.P = 130-132 °C, ^{1}H NMR ($CDCl_3$): 1.8-1.1 (m, 11H, cyclohexane hydrogens), 2.5 (s, 3H, CH_3CO), 3.7 (s, 3H, OCH_3), 5.3 (d, 1H, C5-H), 7.3-7.1 (m, 5H, 1NH + 4H for aromatic protons underneath); ^{13}C NMR ($CDCl_3$): 26.1 (**CH_3**CO), 40.1-24.2 (cyclohexane carbons), 52.7 (O**CH_3**), 87.8 (C- 5), 141.6, 131.3, 129.8, 114.5 (aromatic carbons), 147.2 (C=N), 156.3 (CH_3O**C=O**), 189.1 (CH_3**C=O**). IR: cm^{-1} = 2540 (NH), 1711 (OC=O), 1679 (C=O acetyl).

Acknowledgement
The authors wish to thank Dr. Jalal Zahra (university of Jordan) for obtaining the NMR spectra.

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