Oxadiazole, oxadiazine, oxadiazepine, pyrazole and tetrazole derivatives from substituted carbohydrazides

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The condensation of substituted carbohydrazides **1a–e** with a series of electron-poor compounds such as dimethyl but-2-ynediolate (**2**), 1,4-diphenylbut-2-yne-1,4-dione (**3**), 1,4-diphenylbut-2-ene-1,4-dione (**4**), and diethyl diazene-1,2-dicarboxylate (**5**) gave the derivatives of 1,3,4-oxadiazepine, 1,3,4-oxadiazinylacetate, (1,3,4-oxadiazolylidene) ethanone, dibenzoylpyrazole and tetrazolecarboxylate. The reaction mechanisms described the products formation are discussed.

Keywords: substituted carbohydrazides, oxadiazole, oxadiazine, oxadiazepine, pyrazole and tetrazole derivatives

Hydrazine derivatives have been extensively used as useful precursors for synthesis of 1,3,4-oxadiazole,[1-3] triazole,[2-6] triazine,[7,8] pyrazole[9] and indazole[10] derivatives. The reactions of aroylphenylacetylenes with ethyl and phenyl hydrazinecarboxylates have been reported to give ω-aroylacetophenone-*N*-ethoxycarbonyl- and *N*-phenoxycarbonylhydrazones, respectively.[11-15] Al-Hajjar and co-workers[16] subsequently claimed that the previous work was in error and the reaction of aroylphenylacetylenes with *tert*-butyl hydrazinecarboxylate and 2-furylhydrazides gave hydroxydihydropyrazole derivatives. Upon heating this pyrazole derivative with acetic anhydride followed by hydrolysis afforded 5(3)aryl-3(5)phenylpyrazoles.[16]

Such study is expected to shed further light on the mechanism of this reaction, and on the structure of the products. We suspected that the anions of substituted carbohydrazides would be at a high energy level and might show interesting chemical behaviour. We report herein the results of our recent investigations on the addition of the dienophiles **2–4** to substituted carbohydrazides **1a–e**.

When the condensation of **1a–e** with **2** was carried out in refluxing methanol, methyl 7-oxa-2-substituted-4,7-dihydro-1,3,4-oxadiazepine-5-carboxylate **6a–e** and methyl 2-(6-oxo-2-substituted-6*H*-1,3,4-oxadiazin-5-yl)acetate **9a–c** (Scheme 1), were obtained.

The addition of the terminal hydrazide nitrogen of **1a–e** on the C≡C triple bond of **2**, may generate the adducts **A** and/or **B** (Scheme 1), capable of releasing MeOH. Thus, the structures of products **6a–e** and **9a–e** need to be derived from the two suitable precursors out of the options **A** and **B**.

Three isomeric structures **6–8** resulting from precursor **A**. Structures **7** and **8** could be ruled out on the basis of ^{1}H NMR, ^{13}C NMR and the fragmentation ions in the mass spectrum of methyl-2-(1*H*-indol-2-yl)-7-oxo-4,7-dihydro-1,3,4-oxadiazepine-5-carboxylate (**6e**) at *m/z* 285, 226, 142, 99, 92, 59 and 44. As shown in Scheme 1, **6e** fits best to all the spectroscopic data (see Experimental).

Methyl 2-(6-oxo-2-substituted-6*H*-1,3,4-oxadiazin-5-yl) acetate **9a–e**, were obtained as a characteristically yellow colour. The molecular structure of **9e** is supported by the following findings:

- The gross formula $C_{14}H_{11}N_3O_4$ represents a product from one molecule of **1e** and one molecule of **2** with the loss of one molecule of MeOH.
- The presence of acetate-CH_2 (δ_c = 31.11 ppm) and the absence of oxadiazine-NH rules out the presence of isomeric enamine structure **10e**.
- ^{1}H NMR spectrum shows the presence of indole-NH at (δ_H = 11.78 ppm).
- In ^{13}C NMR spectrum of **9e**, the oxo group of oxadiazinone (δ_c = 165.73 ppm) and the carbonyl ester function (δ = 167.66 ppm) were observed.
- The mass spectrum shows fragments at *m/z* 212 (representing substituted oxadiazinyl residue).

It has been reported that in imine–enamine tautomerism, the imine form is generally predominant over the enamine.[17,18] One of the authors has shown previously that some acetate derivatives of a naturally-occuring pteridine, *i.e.* alkyl isoxanthopterin-6-acetates consist exclusively of the imine form.[19]

The addition of substituted carbohydrazides **1a–e** to another type of triple bond dienophile (1,4-diphenylbut-2-yne-1,4-dione **3**) afforded the formation of oxadiazolylacetophenone **12a–e** and 3-substituted 4,5-dibenzoyl-1H-pyrazole **14a–e** as condensation products.

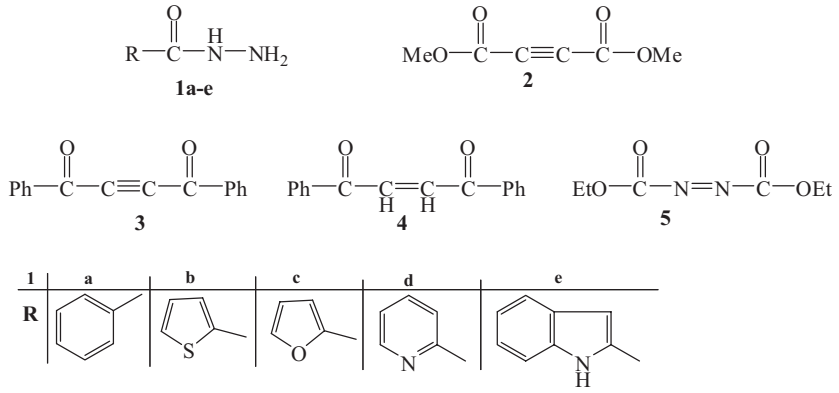

Fig. 1

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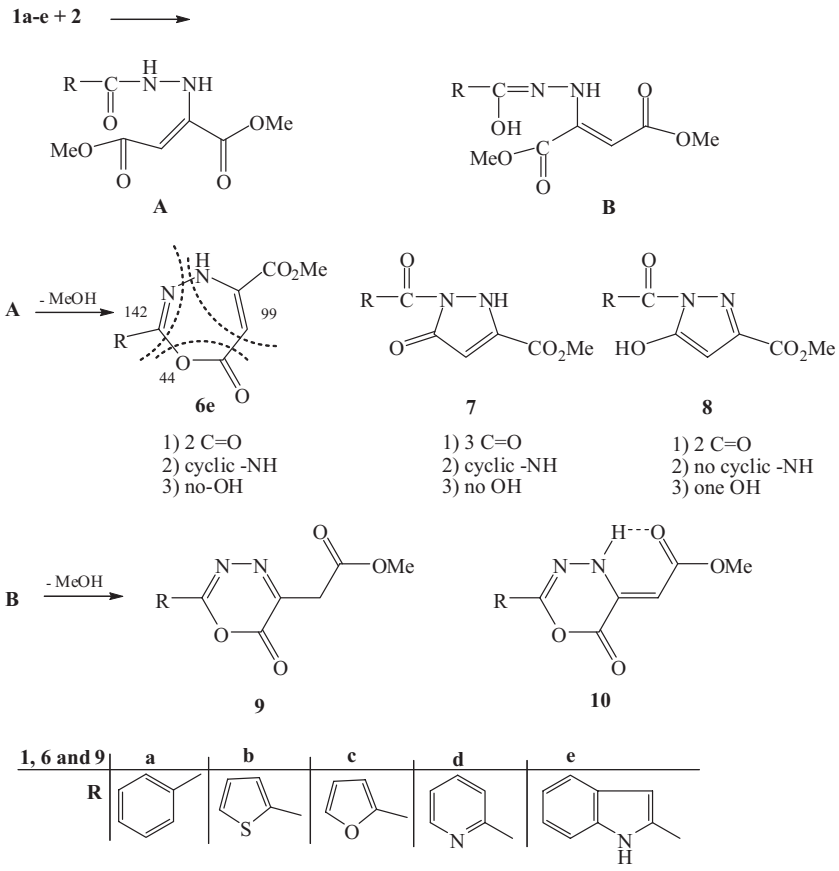


Scheme 1

The IR and NMR spectra of **12a–e** distinguished between the enamine form **12a–e** and the imine form **13**. The side chain carbonyl in the imine form should give a normal carbonyl absorption, but showed a band in the region 1660–1665 cm^{-1}. The shift to lower frequencies is consistent with the occurrence of an *α,β*-unsaturated carbonyl group probably in hydrogen bonding detected by IR (in dilute CCl_4) and ^1H NMR (see Experimental).

The enamine structures **12a–e** were further supported by ^1H NMR spectra. In **12b** the signals of =CH, instead of CH_2- appeared together with those of hydrogen bonded –NH at lower field δ = 5.90–6.06 ppm. The decoupled carbon spectrum of **12b** showed signals at δ = 70.14, 155.96, 172.06 and 190.26 assigned to ylidenic–CH, oxadiazole–C-5, and carbonyl group, respectively. The presence of =CH group was also evident from the ^{13}C DEPT NMR spectrum exhibiting positive signals at δ = 70.14 ppm.

The second zone with yellow colour containing compounds 5-substituted-3,4-dibenzoyl pyrazoles **14a–e**, the IR spectrum of **14b** showed characteristic absorption to NH group at 3255 cm^{-1} and strong vibrational of C=O group at 1655 cm^{-1}. The ^1H NMR spectrum of **14b** showed one broad signal centred at δ_H = 13.82 ppm due to pyrazole –NH. In its ^{13}C NMR spectrum, pyrazole-C-4, C-3 and C-5 resonate at δ = 104.71, 143.55 and 148.86 ppm, respectively. The alternative structures **15** and **16** could also ruled out on the basis of IR, ^1H NMR and ^{13}C NMR.

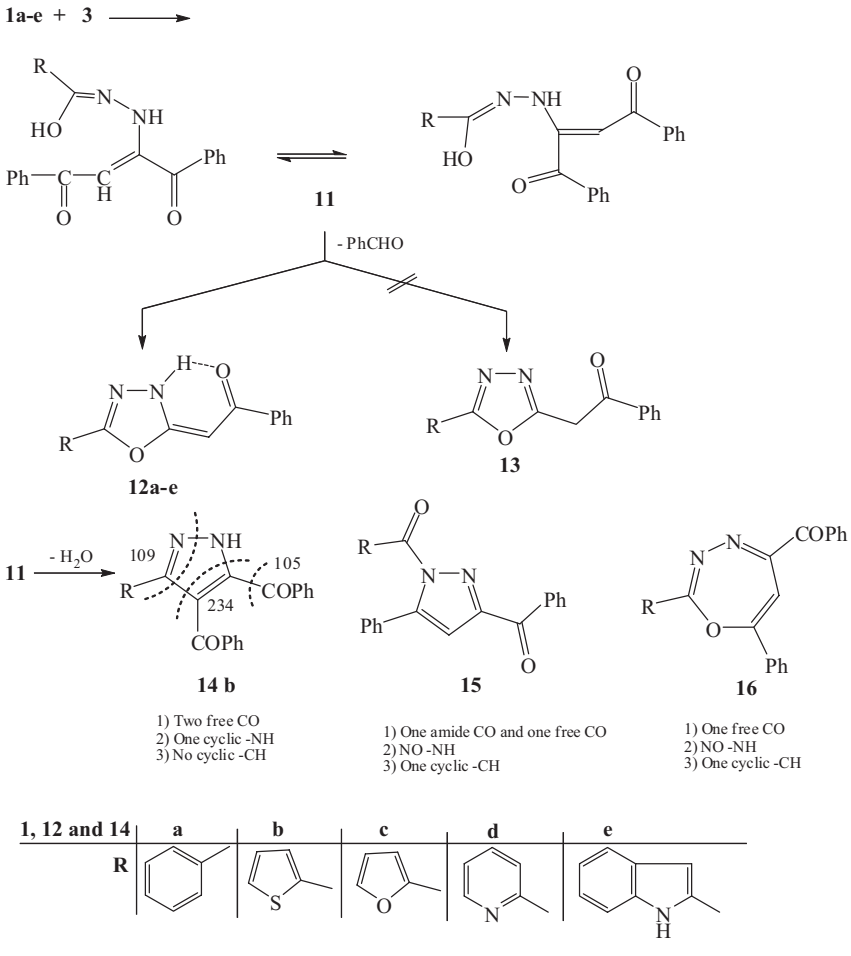
On the other hand, the reaction of substituted carbohydrazides **1a–e** with 1,4-diphenylbut-2-ene-1,4-dione (**4**) in refluxing acetic acid produced the 3-phenyl-4-substituted pyrazoles **18a–e** in 74-81% yields (Scheme 3).

Mass spectra and elemental analyses stablished the molecular formula of **18b** as $C_{14}H_{10}N_2OS$. The IR spectrum of **18b** shows absorption characteristic of NH and CO groups at ν = 3260 and 1660 cm^{-1}, respectively. The low field pyrazole-NH group is present at δ_H = 13.79 ppm. A signal around 148.64 ppm, in ^{13}C NMR spectra due to pyrazole-CH further supports the structure assigned to **18b**. The decoupled carbon spectrum of **18b** showed signals at δ_C = 112.14, 151.96 and 196.16 due to pyrazole-C-4, C-5 and C=O respectively, besides the thiophene carbons. Furthermore, the following common features of the fragmentation patterns lend support the assigned structure: Loss of PhCO giving intense (M^+-105) ions common in the spectra of all five compounds. It has been reported that 4-aroyl-3,5-diarylpyrazoles were prepared from the condensation of 3-aroyl-2-arylchromones with hydrazine hydrate.[20,21]

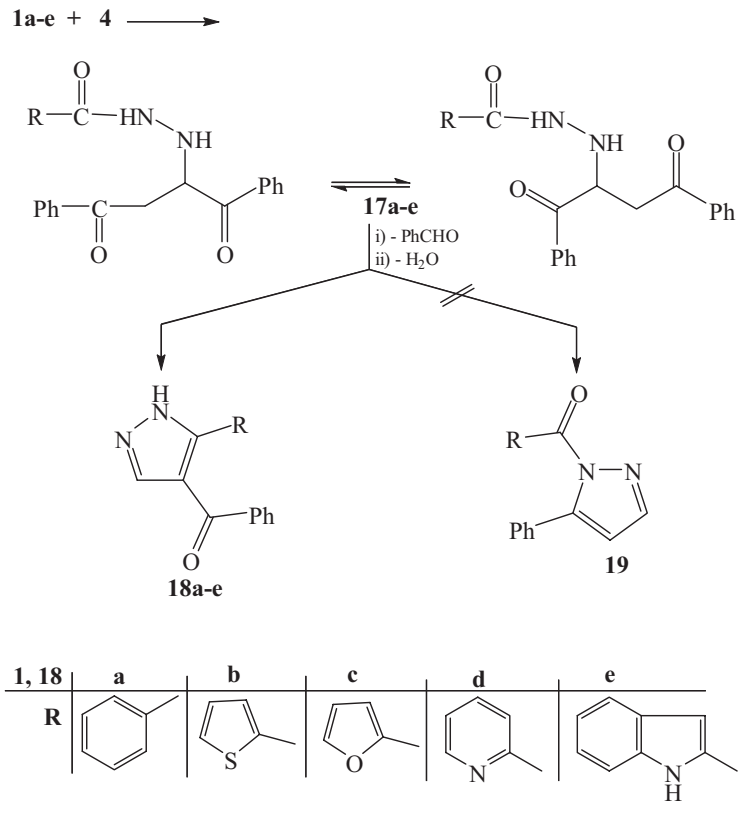
Diethyl diazene-1,2-dicarboxylate (**5**) plays an important role in the cycloaddition reactions such as ene reactions.[22] Recently, triazolopyridines and triazolopyrimidines have been synthesised from **5** and acylated hydrazinopyridines and pyrimidines using a modified Mitsunobu reactions.[23]

In the light of the forementioned promising results, our attention turned to the reactions of substituted carbohydrazides **1a–e** with diethyl diazene-1,2-dicarboxylate (**5**) (Scheme 4). The reaction of **1a–e** with **5** was carried out in acetic acid at reflux temperature and afforded ethyl 5-substituted-*1H*-tetrazole-1-carboxylate **22** (Scheme 4).

Mass spectroscopy and elemental analysis proved the molecular formula of **22e** as $C_{12}H_{11}N_5O_2$. The IR spectrum showed the presence of indole-NH at ν = 3290 cm^{-1}, sharp band at 1720 cm^{-1} characteristic of carbonyl ester and at 1625 cm^{-1} due to C=N. The ^1H NMR spectrum clearly shows the ethoxy group at 1.25 and 4.18 ppm (*J* = 7.28 Hz). The absence of a ^{13}C NMR C=O signal of acyl hydrazine and the presence of an ester C=O signal at (δ_C = 168.34 ppm) as well as one C=N resonate at (δ_C = 158.46 ppm) in addition to indole-carbons points to the structure **22e** as assigned.



Scheme 2



Scheme 3

The EI mass spectrum of **22e** is characterised by molecular ion of low intensity and loss of 45 amu (representing C_2H_5O). The resulting fragment ions undergo loss of 28 amu (probably N_2 or CO group), followed by loss of 142 amu (most likely the R–CN group).

The alternative structure **24** (Scheme 4) could be ruled out according to the spectral data (see Experimental).

It has been reported that N=N–C=O grouping of diethyl diazene-1,2-dicarboxylate **5** plays the role of diene, a typical example being indene, which also furnishes an oxadiazine with **5**.[24,25] On the other hand, any [$\pi^4 + \pi^2$] cycloadditions of **5** to dehydrogenated **1a–e** are not suggested to occur from the nature of the product formed. Recently, sterically hindered 1,5-disubstituted tetrazoles have been synthesised.[26]

Experimental

All melting points were recorded on a Gallenkamp apparatus using open glass capillaries. IR spectra were run on a Shimadzu 408 spectrometer using potassium bromide pellets (CCl_4 in one case). A Bruker AM400 instrument has been used to determine ^{1}H NMR (400.13 MHz) and ^{13}C NMR (100.6 MHz) spectra, assignments of carbon resonances have been supported by DEPT experiments. The NMR samples were dissolved in dimethyl sulfoxide-d_6 solutions, chemical shifts are expressed as δ (ppm) with tetramethylsilane as internal reference, s = singlet, t = triplet, q = quartet, m = multiplet and b = broad. Coupling constants were expressed in Hz. Mass spectra were recorded on Varian MAT 311 instrument in EI mode (70 eV) ionisation energy. Elemental analyses were determined by Microanalytical Centre, Cairo University, Egypt. Preparative layer chromatography (PLC) used air dried 1.0-mm thick layers of slurry applied silica gel, Merck Pf_{254} on 48 cm wide and 20 cm high glass plates using the solvents listed. Zones were detected by quenching of indicator fluorescence upon exposure to 254 nm light and eluted with acetone.

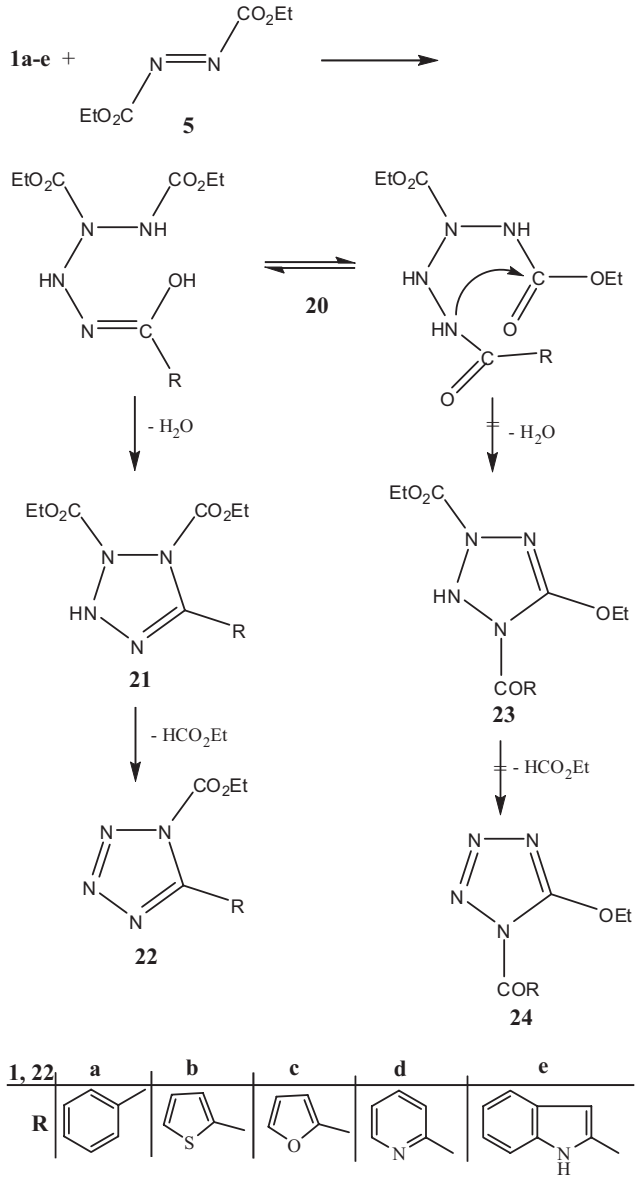
Starting materials

Substituted carbohydrazides **1b–e** were prepared according to published procedures,[27-31] as were thiophene-2-carbohydrazide **(1b),** m.p. 135–137°C (lit.[27] 134–136°C); furan-2-carbohydrazide **(1c)**, m.p. 77–79 (lit.[28] 78°C); pyridine-2-carbohydrazide **(1d)**, m.p. 136–138°C (lit.[29] 137°C); indole-2-carbohydrazide **(1e),** m.p. 243–245°C (lit.[3,30,31] 246°C) and benzohydrazide **(1a)** (Aldrich) was used as received.

Reaction of substituted carbohydrazides **1a–e** *with dimethyl but-2-ynedioate* **(2)**: A mixture of dimethyl but-2-ynedioate **(2)** (284 mg, 2 mmol) and substituted carbohydrazides **1a–e** (1.0 mmol) was heated at reflux in methanol (70 ml) for 7–11 hours (the reaction was followed by TLC analysis). The solvent was evaporated *in vacuo* and the residue was subjected to PLC using toluene/ethyl acetate (2 : 1) as eluent to give numerous zones, two of which (with high intensity) were removed and extracted. The fastest moving zone contained the oxadiazine derivatives **9a–e**, the second zone contained the oxadiazepine derivatives **6a–e**. Extraction of the zones with acetone and concentration gave compounds **6a–e** and **9a–e** which crystallised from a suitable solvent, afforded pure crystals.

Methyl 7-oxo-2-phenyl-4,7-dihydro-1,3,4-oxadiazepine-5-carboxylate **(6a)**: Pale yellow crystals (0.16 g, 65%), m.p. 169–171°C (ethanol). IR (KBr): 3365 (NH), 1745, 1720 (CO), 1630 (C=N), 1610 (Ar-C=C). ^{1}H NMR (DMSO-d_6): δ = 3.72 (s, 3H, OCH_3), 5.91 (s, 1H, oxadiazepine–CH), 6.87 (br, 1H, oxadiazepine–NH), 7.47–7.96 (m, 5H, ArH). ^{13}C NMR (DMSO-d_6): δ = 51.77 (CH_3O), 105.83 (C-6), 128.26, 129.43, 130.66 (ArCH), 131.72 (ArC), 155.81 (C-2), 159.12 (C-5), 166.14 (CO of ester), 170.12 (C-7). MS (*m/z*,**%**): 246 (M^+, 23), 187 (33), 102 (51), 99 (63), 91 (24), 77 (100), 59 (64), 44 (58). $C_{12}H_{10}N_2O_4$ (246.22): Calcd; C, 58.54; H, 4.09; N, 11.38. Found C, 58.71; H, 3.96; N, 11.21.

Methyl 7-oxo-2-(thiophen-2-yl)-4,7-dihydro-1,3,4-oxadiazepine-5-carboxylate **(6b)**: Pale yellow crystals (0.174 g, 64%), m.p. 192–194°C (acetonitrile). IR (KBr): 3370 (NH), 1740, 1720 (CO), 1620 (C=N), 1605 (ArC=C). ^{1}H NMR (DMSO-d_6): δ = 3.75 (s, 3H, OCH_3), 5.88 (s, 1H, oxadiazepine–CH), 6.92 (br, 1H, oxadiazepine–NH), 7.26–7.84 (m, 3H, thiophene–CH). ^{13}C NMR (DMSO-d_6): δ = 51.82 (CH_3O), 105.79 (C-6), 126.81, 127.62, 127.44 (thiophene–CH), 128.96 (thiophene–C), 155.76 (C-2), 158.83 (C-5), 166.27 (CO of ester), 170.28 (C-7). MS (*m/z*,**%**): 252 (M^+, 41), 222 (19),193 (26), 109 (74), 99 (41), 59 (100), 44 (72). $C_{10}H_8N_2O_4S$ (252.25): Calcd; C, 47.61; H, 3.20; N, 11.11; S, 12.71. Found C, 47.82; H, 3.04; N, 10.92; S, 12.89.



Scheme 4

Methyl 7-oxo-2-(furan-2-yl)-4,7-dihydro-1,3,4-oxadiazepine-5-carboxylate **(6c)**: Pale yellow crystals (0.149 g, 63%), m.p. 155–156°C (acetonitrile). IR (KBr): 3370 (NH), 1735, 1715 (CO), 1630 (C=N), 1080 (C–O–C). ^{1}H NMR (DMSO-d_6): δ = 3.77 (s, 3H, OCH_3), 5.89 (s, 1H, oxadiazepine–CH), 6.90 (br, 1H, oxadiazepine–NH), 7.19–7.71 (m, 3H, furan–H). ^{13}C NMR (DMSO-d_6): δ = 52.03 (CH_3O), 105.78 (C-6), 126.63, 127.11, 141.18 (furan–CH), 143.66 (furan–C), 155.74 (C-2), 158.86 (C-5), 166.24 (CO of ester), 170.16 (C-7). MS (*m/z*,**%**): 236 (M^+, 37), 177 (43), 99 (22), 93 (100), 59 (46), 44 (28). $C_{10}H_8N_2O_5$ (236.18): Calcd; C, 50.85; H, 3.41; N, 11.86. Found C, 51.07; H, 3.23; N, 12.08.

Methyl 7-oxo-2-(pyridin-2-yl)-4,7-dihydro-1,3,4-oxadiazepine-5-carboxylate **(6d)**: Pale yellow crystals (0.163 g, 66%), m.p. 183–185°C (methanol). IR (KBr): 3360 (NH), 1745, 1720 (CO), 1625 (C=N), 1610 (Ar–C=C). ^{1}H NMR (DMSO-d_6): δ = 3.74 (s, 3H, OCH_3), 5.85 (s, 1H, oxadiazepine–CH), 6.93 (br, 1H, oxadiazepine–NH), 7.54–8.23 (pyridine–H). ^{13}C NMR (DMSO-d_6): δ = 51.89 (CH_3O), 105.81 (C-6), 126.84, 127.45, 132.12, 146.17 (pyridine–CH), 149.22 (pyridine–C), 155.82 (C-2), 158.94 (C-5), 166.19 (CO of ester), 170.28 (C-7). MS (*m/z*,**%**): 247 (M^+, 21), 216 (11), 188 (34), 104 (41), 99 (22), 59 (84), 44 (100). $C_{11}H_9N_3O_4$ (247.21): Calcd; C, 53.44; H, 3.67; N, 17.00. Found C, 53.61; H, 3.84; N, 16.81.

Methyl 7-oxo-2-(1H-indol-2-yl)-4,7-dihydro-1,3,4-oxadiazepine-5-carboxylate **(6e)**: Pale yellow crystals (0.182 g, 64%), m.p. 224–

226°C (methanol). IR (KBr): 3335–3370 (NH), 1740, 1715 (CO), 1625 (C=N), 1610 (ArC=C). ^{1}H NMR (DMSO-d_6): δ = 3.76 (s, 3H, OCH_3), 5.91 (s, 1H, oxadiazepine–CH), 6.54 (br, 1H, indole–CH), 6.95 (br, 1H, oxadiazepine–NH), 7.08–7.65 (m, 4H, ArH), 11.61(br, 1H, indole–NH). ^{13}C NMR (DMSO-d_6): δ = 51.97 (CH_3O), 101.22 (indole–CH), 105.84 (thiadiazepine–CH), 125.23 (indole–C-2), 127.16, 127.74, 128.15, 128.66 (ArCH), 130.16, 132.14 (ArC), 155.81 (C-2), 158.90 (C-5), 166.39 (CO of ester), 169.98 (C-7). MS (*m/z*,**%**): 285 (M^+, 37), 226 (19), 142 (54), 99 (48), 92 (66), 77 (100), 59 (61), 44 (41). $C_{14}H_{11}N_3O_4$ (285.25): Calcd; C, 58.95; H, 3.89; N, 14.73. Found C, 59.12; H, 4.06; N, 14.56.

Methyl 2-(6-oxo-2-phenyl-6H-1,3,4-oxadiazin-5-yl)acetate **(9a)**: Yellow crystals (0.064 g, 26%), m.p. 157–158°C (acetonitrile). IR (KBr): 1740, 1720 (CO), 1625 (C=N), 1605 (ArC=C). ^{1}H NMR (DMSO-d_6): δ = 2.49 (s, 2H, CH_2), 3.67 (s, 3H, OCH_3), 7.08-7.73 (m, 5H, ArH). ^{13}C NMR (DMSO-d_6): δ = 31.22 (CH_2), 51.74 (CH_3O), 128.17, 128.86, 131.26 (ArCH), 132.14 (Ar-C), 161.65 (C-5), 163.84 (C-2), 165.71 (C-6), 167.56 (CO of ester). MS (*m/z*,**%**): 246 (M^+, 26), 215 (42), 173 (37), 129 (19), 103 (64), 77 (100), 65 (57), 44 (51). $C_{12}H_{10}N_2O_4$ (246.22): Calcd; C, 58.54; H, 4.09; N, 11.38. Found C, 58.76; H, 3.87; N, 11.21.

Methyl 2-[6-oxo-2-(thiophen-2-yl)-6H-1,3,4-oxadiazin-5-yl] acetate **(9b)**: Yellow crystals (0.063 g, 25%), m.p. 184–186°C (ethanol). IR (KBr): 1745, 1720 (CO), 1620 (C=N). ^{1}H NMR (DMSO-d_6): δ = 2.46 (s, 2H, CH_2), 3.69 (s, 3H, OCH_3), 7.22–7.82 (m, 3H, thiophene–H). ^{13}C NMR (DMSO-d_6): δ = 31.16 (CH_2), 51.69 (CH_3O), 126.86, 127.28, 127.67 (thiophene–CH), 129.36 (thiophene–C), 161.59 (C-5), 163.76 (C-2), 165.62 (C-6), 167.83 (CO of ester). MS (*m/z*,**%**): 252 (M^+, 46), 179 (51), 151 (27), 109 (64), 83 (26), 44 (100). $C_{10}H_8N_2O_4S$ (252.25): Calcd; C, 47.61; H, 3.20; N, 11.11; S, 12.71. Found C, 47.37; H, 3.11; N, 10.94; S, 12.87.

Methyl 2-[2-(furan-2-yl)-6-oxo-6H-1,3,4-oxadiazin-5-yl]acetate **(9c)**: Pale yellow crystals (0.068 g, 29%), m.p. 149–150°C (ethanol). IR (KBr): 1740, 1710 (CO), 1630 (C=N), 1080 (C–O–C). ^{1}H NMR (DMSO-d_6): δ = 2.46 (s, 2H, CH_2), 3.70 (s, 3H, OCH_3), 7.15–7.72 (m, 3H, furan–H). ^{13}C NMR (DMSO-d_6): δ = 30.94 (CH_2), 51.76 (CH_3O), 126.41, 126.87, 141.53 (furan–CH), 143.74 (furan–C), 161.71 (C-5), 163.77 (C-2), 165.76 (C-6), 167.44 (CO of ester). MS (*m/z*,**%**): 236 (M^+, 21), 205 (24), 163 (19), 93 (100), 44 (51). $C_{10}H_8N_2O_5$ (236.18): Calcd; C, 50.85; H, 3.41; N, 11.86. Found C, 51.08; H, 3.29; N, 12.04.

Methyl 2-[6-oxo-2-(pyridin-2-yl)-6H-1,3,4-oxadiazin-5-yl]acetate **(9d)**: Pale yellow crystals (0.069 g, 28%), m.p. 168–170°C (acetonitrile). IR (KBr): 1735, 1715 (CO), 1630 (C=N). ^{1}H NMR (DMSO-d_6): δ = 2.49 (s, 2H, CH_2), 3.67 (s, 3H, OCH_3), 7.58–8.41 (m, 4H, pyridine–H). ^{13}C NMR (DMSO-d_6): δ = 30.89 (CH_2), 51.83 (CH_3O), 127.39, 127.74, 129.84 (pyridine–CH), 146.22 (pyridine–C-2), 148.41 (pyridine–C-6), 161.63 (C-5), 163.84 (C-2), 165.71 (C-6), 168.12 (CO of ester). MS (*m/z*,**%**): 247 (M^+, 34), 216 (28), 174 (29), 104 (87), 44 (100). $C_{11}H_9N_3O_4$ (247.21): Calcd; C, 53.44; H, 3.67; N, 17.00. Found C, 53.69; H, 3.58; N, 16.78.

Methyl 2-[2-(indol-2-yl)-6-oxo-6H-1,3,4-oxadiazin-5-yl]acetate **(9e)**: Yellow crystals (0.071 g, 25%), m.p. 202–204°C (methanol). IR (KBr): 3375 (NH), 1745, 1715 (CO), 1630 (C=N), 1595 (ArC=C). ^{1}H NMR (DMSO-d_6): δ = 2.48 (s, 2H, CH_2), 3.66 (s, 3H, OCH_3), 6.81 (s, 1H, indole–CH), 7.05–7.71 (m, 4H, ArH), 11.78 (br, 1H, indole–NH). ^{13}C NMR (DMSO-d_6): δ = 31.11 (CH_2), 51.69 (CH_3O), 99.94 (indole–CH), 123.65 (indole-C-2), 126.56, 127.41, 128.33, 128.94 (ArCH), 130.16, 131.44 (ArC), 161.68 (C-5), 163.82 (C-2), 165.73 (C-6), 167.66 (CO of ester). MS (*m/z*,**%**): 285 (M^+, 18), 254 (9), 212 (34), 142 (46), 91 (74), 77 (100), 65 (83), 44 (39). $C_{14}H_{11}N_3O_4$ (285.25): Calcd; C, 58.95; H, 3.89; N, 14.73. Found C, 58.71; H, 4.02; N, 14.91.

Reaction of substituted carbohydrazides **1a–e** *with 1,4-diphenylbut-2-yne-1,4-dione* **(3)**: A mixture of **1a–e** (2.0 mmol) and **3** (234 mg, 1 mmol) was heated at reflux in acetic acid (100 ml) for 5–9 h. The solvent was evaporated *in vacuo* and then subjected to PLC using toluene/ethyl acetate (5:3) as eluent to give two zones the fastest moving zone contained 1-phenyl-2-(5-substituted-1,3,4-oxadiazol-2(3*H*)-ylidene)ethanone **12a–e**, while the slowest moving zone contained the pyrazole derivatives **14a–e**. Extraction of the zones with acetone and concentration gave residues, which were rechromatographed to improve the purification.

1-Phenyl-2-(5-phenyl-1,3,4-oxadiazol-2(3H)-ylidene)ethanone **(12a)**: Compound **12a** was obtained as pale yellow crystals (0.069 g, 26%), m.p. 186–188°C (ethanol). IR (KBr): 3310 (NH), 1665 (CO), 1610 (ArC=C), 1085 (C–O–C); (CCl_4, 10^{-3} M, d = 3 cm): 3290 (NH), 1655 (CO). ^{1}H NMR (DMSO-d_6): δ = 5.96 (s, 1H, ylidenic–H), 7.28–7.76 (m, 10H, ArH), 13.96 (br, 1H, oxadiazole–NH). ^{13}C NMR (DMSO-d_6): δ = 69.63 (ylidenic–CH), 128.96, 129.21, 129.37, 129.95, 130.16, 130.29 (ArCH), 132.67, 137.86 (ArC), 156.14 (C-5), 171.88 (C-2), 190.16 (CO). MS (*m/z*,**%**): 264 (M^+, 34), 159 (43), 131 (29), 105 (100), 77 (74), 65 (36), 42 (47). $C_{16}H_{12}N_2O_2$ (264.28): Calcd; C, 72.72; H, 4.58; N, 10.60. Found C, 72.93; H, 4.46; N, 10.38.

1-Phenyl-2-[5-(thiophen-2-yl)-1,3,4-oxadiazol-2(3H)-ylidene] ethanone **(12b)**: Pale yellow crystals (0.068 g, 25%), m.p. 207–209°C (acetonitrile). IR (KBr): 3325 (NH), 1660 (CO), 1600 (ArC=C), 1080 (C–O–C). ^{1}H NMR (DMSO-d_6): δ = 5.90 (s, 1H, ylidenic–H), 7.33–7.87 (m, 8H, Ar and thiophene–H), 14.00 (br, 1H, oxadiazole–NH). ^{13}C NMR (DMSO-d_6): δ = 70.14 (ylidenic–CH), 126.14, 127.22, 127.45, 129.36, 129.95, 130.12 (ArCH and thiophene–CH), 131.26, 137.81 (ArC and thiophene–C), 155.96 (C-5), 172.06 (C-2), 190.26 (CO). MS (*m/z*,**%**): 270 (M^+, 33), 165 (42), 137 (28), 105 (100), 95 (26), 77 (66). $C_{14}H_{10}N_2O_2S$ (270.31): Calcd; C, 62.21; H, 3.73; N, 10.36; S, 11.86. Found C, 61.98; H, 3.87; N, 10.54; S, 11.69.

2-[5-(Furan-2-yl)-1,3,4-oxadiazol-2-(3H)ylidene]-1-phenyl-ethanone **(12c)**: Compound **12c** was obtained as pale yellow crystals (0.074 g, 29%), m.p. 168–170°C (ethanol). IR (KBr): 3315 (NH), 1665 (CO), 1600 (ArC=C), 1090 (C–O–C). ^{1}H NMR (DMSO-d_6): δ = 6.06 (s, 1H, ylidenic–H), 7.28–7.81 (m, 8H, ArH and furan–H), 13.95 (br, 1H, oxadiazole–NH). ^{13}C NMR (DMSO-d_6): δ = 70.16 (ylidenic–CH), 127.18, 127.59, 129.46, 129.92, 131.12, 141.56 (ArCH and furan–CH), 137.55, 144.67 (ArC and furan–C), 155.96 (C-5), 172.05 (C-2), 189.96 (CO). MS (*m/z*,**%**): 254 (M^+, 27), 149 (45), 121 (23), 105 (96), 77 (100), 65 (83). $C_{14}H_{10}N_2O_3$ (254.24): calcd; C, 66.14; H, 3.96; N, 11.02. Found C, 65.91; H, 4.09; N, 10.87.

1-Phenyl-2-[5-(pyridin-2-yl)-1,3,4-oxadiazol-2(3H)-ylidene] ethanone **(12d)**: Compound **12d** was obtained as yellow crystals (0.074 g, 28%), m.p. 191–193°C (acetonitrile). IR (KBr): 3325 (NH), 1665 (CO), 1600 (ArC=C), 1080 (C–O–C). ^{1}H NMR (DMSO-d_6): δ = 5.95 (s, 1H, ylidenic–H), 7.38–8.46 (m, 9H, ArH and pyridine–H), 13.94 (br, 1H, thiadiazole–NH). ^{13}C NMR (DMSO-d_6): δ = 70.28 (ylidenic–CH), 126.24, 128.33, 129.47, 129.81, 130.12 (ArCH and pyridine–CH), 137.84 (ArC), 145.67 (pyridine–C-2), 148.12 (pyridine–CH-6), 155.16 (C-5), 171.82 (C-2), 191.11 (CO). MS (*m/z*,**%**): 265 (M^+, 27), 160 (39), 104 (68), 105 (100), 77 (89), 65 (74). $C_{15}H_{11}N_3O_2$ (265.27): Calcd; C, 67.92; H, 4.18; N, 15.84. Found C, 68.11; H, 4.08; N, 15.65.

2-[5-(1H-Indol-2-yl)-1,3,4-oxadiazol-2(3H)-ylidene]-1-phenyl-ethanone **(12e)**: Compound **12e** was obtained as yellow crystals (0.076 g, 25%), m.p. 231–233°C (acetonitrile). IR (KBr): 3360, 3310 (NH), 1660 (CO), 1595 (ArC=C), 1080 (C–O–C). ^{1}H NMR (DMSO-d_6): δ = 6.00 (s, 1H, ylidenic–H), 6.48 (s, 1H, indole–CH), 7.17–7.75 (m, 9H, ArH), 11.72 (br, 1H, indole–NH), 13.94 (br, 1H, oxadiazole–NH). ^{13}C NMR (DMSO-d_6): δ = 70.71 (ylidenic–CH), 101.16 (indole–CH), 122.28 (indole–C2), 127.18, 127.86, 128.54, 128.77, 129.37, 129.96, 130.12 (ArCH), 131.33, 132.11, 137.84 (ArC), 155.81 (C-5), 171.83 (C-2), 190.28 (CO). MS (*m/z*,**%**): 303 (M^+, 34), 198 (36), 170 (21), 128 (31), 116 (17), 105 (100), 91 (41), 77 (67), 65 (54). $C_{18}H_{13}N_3O_2$ (303.31): Calcd; C, 71.28; H, 4.32; N, 13.85. Found C, 71.06; H, 4.24; N, 14.12.

5-Phenyl-3,4-dibenzoyl-2H-pyrazole **(14a)**: Yellow crystals (0.204 g, 58%), m.p. 246–248°C (acetonitrile). IR (KBr): 3260 (NH), 1655 (CO), 1600 (ArC=C). ^{1}H NMR (DMSO-d_6): δ = 7.21–7.83 (m, 15H, ArH), 13.82 (br, 1H, pyrazole–NH). ^{13}C NMR (DMSO-d_6): δ = 104.57 (C-4), 127.52, 128.36, 128.73, 128.85, 128.96, 129.34, 129.74, 129.85, 129.95 (ArCH), 132.74, 133.14, 133.46 (ArC), 143.74 (C-5), 149.66 (C-3), 191.33, 196.36 (CO). MS (*m/z*,**%**): 352 (M^+, 26), 234 (34), 118 (28), 105 (100), 77 (83), 65 (54). $C_{23}H_{16}N_2O_2$ (352.39): Calcd; C, 78.39; H, 4.58; N, 7.95. Found C, 78.55; H, 4.46; N, 8.12.

5-Thiophenyl-3,4-dibenzoyl-2H-pyrazole **(14b)**: Yellow crystals (0.205 g, 57%), m.p. 261–263°C (acetonitrile). IR (KBr): 3255 (NH), 1655 (CO), 1620 (C=N), 1600 (ArC=C). ^{1}H NMR (DMSO-d_6): δ = 7.14–7.82 (m, 13H, ArH and thiophene–H), 13.82 (br, 1H, pyrazole–NH). ^{13}C NMR (DMSO-d_6): δ = 104.71 (C-4), 125.96, 127.64, 127.93, 128.65, 128.96, 129.75, 130.23, 130.35 (ArCH and thiophene–CH), 131.44, 131.51 (ArC), 140.11 (thiophene–C-2), 143.55 (C-5), 148.86 (C-3), 190.74, 196.33 (CO). MS (*m/z*,**%**): 358 (M^+, 27), 253 (21), 234 (37), 124 (29), 105 (89), 77 (100), 65 (78). $C_{21}H_{14}N_2O_2S$ (358.41): Calcd; C, 70.37; H, 3.94; N, 7.82; S, 8.95. Found C, 70.19; H, 4.07; N, 7.96; S, 9.11.

5-(Furan-2-yl)-3,4-dibenzoyl-2H-pyrazole **(14c)**: Yellow crystals (0.188 g, 55%), m.p. 235–237°C (ethanol). IR (KBr): 3270 (NH), 1660 (CO), 1615 (C=N), 1595 (ArC=C), 1085 (C–O–C). ^{1}H NMR

(DMSO-d_6): δ = 7.17–7.76 (m, 13H, ArH and furan–H), 13.78 (br, 1H, pyrazole–NH). ^{13}C NMR (DMSO-d_6): δ = 104.79 (C-4), 126.18, 127.33, 128.76, 128.95, 129.54, 129.77, 130.14, 130.65 (ArCH and furan–CH), 141.46 (furan–C-5), 143.31 (C-5), 149.22 (C-3), 150.11 (furan–C-2), 192.0, 195.84 (CO). MS (*m/z*,**%**): 342 (M^+, 18), 234 (39), 108 (19), 105 (100), 77 (64), 65 (59). $C_{21}H_{14}N_2O_3$ (342.35): Calcd; C, 73.68; H, 4.12; N, 8.18. Found C, 73.85; H, 3.98; N, 7.94.

5-(Pyridin-2-yl)-3,4-dibenzoyl-2H-pyrazole **(14d)**: Yellow crystals (0.201 g, 57%), m.p. 254–256°C (methanol). IR (KBr): 3265 (NH), 1660 (CO), 1625 (C=N), 1610 (ArC=C). ^{1}H NMR (DMSO-d_6): δ = 7.32–8.26 (m, 14H, ArH and pyridine–H), 13.78 (br, 1H, pyrazole–NH). ^{13}C NMR (DMSO-d_6): δ = 105.12 (C-4), 125.88, 126.29, 128.53, 128.94, 129.72, 130.19, 130.57 (ArCH and pyridine–CH), 133.14 (pyridine–CH-4), 142.67 (C-5), 148.55 (C-3), 149.77 (pyridine–CH-6), 155.48 (pyridine–C-2), 190.89, 196.42 (CO). MS (*m/z*,**%**): 353 (M^+, 42), 248 (22), 234 (37), 119 (25), 105 (100), 77 (81), 65 (67). $C_{22}H_{15}N_3O_2$ (353.37): Calcd; C, 74.78; H, 4.28; N, 11.89. Found C, 74.59; H, 4.42; N, 12.09.

5-(1H-Indol-2-yl)-3,4-dibenzoyl-2H-pyrazole **(14e)**: Yellow crystals (0.219 g, 56%), m.p. 289–291°C (methanol). IR (KBr): 3345, 3270 (NH), 1655 (CO), 1620 (C=N), 1595 (ArC=C). ^{1}H NMR (DMSO-d_6): δ = 6.48 (s, 1H, indole–CH), 7.16–7.86 (m, 14H, ArH), 11.65 (br, 1H, indole–NH), 13.77 (br, 1H, pyrazole–NH). ^{13}C NMR (DMSO-d_6): δ = 100.46 (indole–CH), 105.11 (C-4), 126.22, 126.41, 127.28, 128.74, 128.97, 130.26, 130.54 (ArCH), 131.33, 134.28, 134.37, 135.27 (ArC), 136.27 (indole–CH-2), 143.27 (C-5), 148.89 (C-3), 190.86, 196.49 (CO). MS (*m/z*,**%**): 391 (M^+, 43), 286 (34), 181 (18), 105 (100), 91 (89), 77 (82), 65 (64). $C_{25}H_{17}N_3O_2$ (391.42): Calcd; C, 76.71; H, 4.38; N, 10.74. Found C, 76.92; H, 4.21; N, 10.58.

The reaction of substituted carbohydrazides **1a**–**e** *with 1,4-diphenylbut-2-ene-1,4-dione* **(4)**: To a magnetically stirred solution of **1a**–**e** (2 mmol) in glacial acetic acid (50 ml), 1,4-diphenylbut-2-ene-1,4-dione (236 mg, 1 mmol) was added. The mixture was heated under reflux for 12–18 h (the reaction was followed by TLC analysis). The solvent was removed under reduced pressure and the residue was purified by plc using toluene/ethyl acetate (3:1) to afford the products **18a**–**e**.

3-Phenyl-4-benzoyl-2H-pyrazole **(18a)**: Pale yellow crystals (0.193 g, 78%), m.p. 144–146°C (ethanol). IR (KBr): 3245 (NH), 1665 (CO), 1625 (C=N), 1585 (ArC=C). ^{1}H NMR (DMSO-d_6) δ: 6.95–7.92 (m, 11H, ArH and pyrazole–CH), 13.82 (br, 1H, pyrazole–NH). ^{13}C NMR (DMSO-d_6) δ: 112.26 (C-4), 126.84, 127.26, 128.65, 128.71, 129.66, 129.89 (ArCH), 132.88, 133.26 (ArC), 148.54 (C-5), 152.18 (C-3), 195.84 (CO). MS (*m/z*,%): 248 (M^+, 21), 143 (42), 105 (100), 103 (36), 77 (78), 65 (55). $C_{16}H_{12}N_2O$ (248.28): Calcd; C, 77.40; H, 4.87; N, 11.28. Found C, 77.19; H, 5.02; N, 11.45.

3-Phenyl-4-(thiophen-2-yl)-2H-pyrazole **(18b)**: Yellow crystals (0.206 g, 81%), m.p. 158–160°C (acetonitrile). IR (KBr): 3260 (NH), 1660 (CO), 1630 (C=N), 1600 (ArC=C). ^{1}H NMR (DMSO-d_6) δ: 7.08–7.95 (m, 9H, ArH, thiophene–H and pyrazole–CH), 13.79 (br, 1H, pyrazole–NH). ^{13}C NMR (DMSO-d_6) δ: 112.14 (C-4), 126.84, 127.55, 128.41, 128.98, 129.56, 129.83 (ArCH and thiophene–CH), 132.57 (ArC), 138.96 (thiophene–C-2), 148.64 (C-5), 151.96 (C-3), 196.16 (CO). MS (*m/z*,%): 254 (M^+, 34), 149 (24), 109 (39), 105 (87), 77 (100), 65 (74). $C_{14}H_{10}N_2OS$ (254.31): Calcd; C, 66.12; H, 3.96; N, 11.02; S, 12.61. Found C, 65.95; H, 4.07; N, 10.86; S, 12.83.

4-(Furan-2-yl-3-phenyl)-2H-pyrazole **(18c)**: Compound **18c** was obtained as yellow crystals (0.176 g, 74%), m.p. 122–123°C (ethanol). IR (KBr): 3250 (NH), 1660 (CO), 1630 (C=N), 1590 (ArC=C), 1085 (C–O–C). ^{1}H NMR (DMSO-d_6) δ: 6.98–7.94 (m, 9H, ArH, furan–H and pyrazole–CH), 13.75 (br, 1H, pyrazole–NH). ^{13}C NMR (DMSO-d_6) δ: 111.98 (C-4), 125.87, 127.12, 128.94, 129.57 (ArCH and furan–CH), 132.54 (ArC), 143.26 (furan–C-5), 148.66 (C-5), 152.11 (C-3), 158.26 (furan–C-2), 195.87 (CO). MS (*m/z*,%): 238 (M^+, 22), 133 (29), 105 (100), 93 (57), 77 (86), 65 (64). $C_{14}H_{10}N_2O_2$ (238.24): Calcd; C, 70.58; H, 4.23; N, 11.76. Found C, 70.77; H, 4.55; N, 11.54.

3-Phenyl-4-(pyridin-2-yl)-2H-pyrazole **(18d)**: Yellow crystals (0.197 g, 79%), m.p. 185–187°C (methanol). IR (KBr): 3265 (NH), 1665 (CO), 1625 (C=N), 1590 (ArC=C). ^{1}H NMR (DMSO-d_6) δ: 7.12–8.33 (m, 10H, ArH, pyridine–H and pyrazole–H), 13.81 (br, 1H, pyrazole–NH). ^{13}C NMR (DMSO-d_6) δ: 111.94 (C-4), 126.62, 126.97, 127.88, 129.16, 130.26, 132.44 (ArCH and pyridine–CH), 133.74 (ArC), 148.14 (C-5), 149.23 (pyridine–C6), 151.26 (C-3), 156.26 (pyridine–C-2), 196.21 (CO). MS (*m/z*,%): 249 (M^+, 31), 144 (18), 104 (76), 105 (100), 77 (64), 65 (59). $C_{15}H_{11}N_3O$ (249.27): Calcd; C, 72.28; H, 4.45; N, 16.86. Found C, 72.49; H, 4.32; N, 17.02.

4-(Indol-2-yl)-3-phenyl-2H-pyrazole **(18e)**: Yellow crystals (0.218 g, 76%), m.p. 197–199°C (methanol). IR (KBr): 3310, 3270 (NH), 1655 (CO), 1630 (C=N), 1600 (ArC=C). ^{1}H NMR (DMSO-d_6) δ: 6.53 (indole–CH), 6.97–7.92 (m, 10H, ArH and pyrazole–CH), 11.68 (br, 1H, indole–NH), 13.82 (br, 1H, pyrazole–NH). ^{13}C NMR (DMSO-d_6) δ: 102.28 (indole–CH), 111.19 (C-4), 125.87, 126.33, 126.76, 127.94, 128.57, 129.23, 130.12 (ArCH), 131.42, 132.26, 133.14 (ArC), 148.23 (C-5), 149.27 (indole–C-2), 152.26 (C-3), 196.17 (CO). MS (*m/z*,%): 287 (M^+, 29), 182 (31), 142 (21), 105 (91), 91 (57), 77 (100), 65 (76). $C_{18}H_{13}N_3O$ (287.32): Calcd; C, 75.25; H, 4.56; N, 14.63. Found C, 75.47; H, 4.43; N, 14.41.

The reaction of substituted carbohydrazides **1a**–**e** *and diethyl diazene-1,2-dicarboxylate* **(5)**: Into a 250 cm^3 two-necked round bottom flask containing a solution of **1a**–**e** (2 mmol) in glacial acetic acid (50 ml), a solution of **5** (0.174 g, 1 mmol) in glacial acetic acid (10 ml) was added dropwise with stirring. The mixture was stirred at room temperature for 1 hour, then reflux for 6–8 h (the reaction was monitored by TLC analysis). The solvent was evaporated under vacuum and the formed solid products were purified by dissolving them in acetone (10 cm^3) and then subjected to preparative layer chromatography (plc) using toluene/ethyl acetate (3:1). The obtained products **22a**–**e** were recrystallised from the stated solvents.

Ethyl 5-phenyl-1H-tetrazole-1-carboxylate **(22a)**: Pale yellow crystals (0.161 g, 74%), m.p. 129–130°C (ethanol). IR (KBr): 3080 (ArCH), 1725 (CO), 1625 (C=N). ^{1}H NMR (DMSO-d_6) δ: 1.24 (t, 3H, CH_3, J = 7.37 Hz), 4.16 (q, 2H, OCH_2, J = 7.37 Hz), 7.31–7.49 (m, 5H, ArH). ^{13}C NMR (DMSO-d_6) δ: 14.06 (CH_3), 62.35 (CH_2O), 127.84, 128.57, 130.22 (ArCH), 132.66 (ArC), 158.44 (C-5), 168.66 (CO). MS (*m/z*,%): 218 (M^+, 42), 173 (36), 145 (29), 103 (72), 77 (100), 65 (64). $C_{10}H_{10}N_4O_2$ (218.21): Calcd; C, 55.04; H, 4.62; N, 25.68. Found C, 54.89; H, 4.74; N, 25.45.

Ethyl 5-(thiophen-2-yl)-1H-tetrazole-1-carboxylate **(22b)**: Yellow crystals (0.157 g, 70%), m.p. 141–142°C (acetonitrile). IR (KBr): 1730 (CO), 1625 (C=N). ^{1}H NMR (DMSO-d_6) δ: 1.23 (t, 3H, CH_3, J = 7.31 Hz), 4.19 (q, 2H, OCH_2, J = 7.31 Hz), 7.17–7.63 (m, 3H, thiophene–H). ^{13}C NMR (DMSO-d_6) δ: 13.97 (CH_3), 62.49 (CH_2O), 127.84, 128.51, 129.33 (thiophene–CH), 141.54 (thiphene–C-2), 158.29 (C-5), 168.54 (CO). MS (*m/z*,%): 224 (M^+, 29), 179 (14), 151 (42), 109 (100), 83 (44), 45 (71). $C_8H_8N_4O_2S$ (224.24): Calcd; C, 42.85; H, 3.60; N, 24.99; S, 14.30. Found C, 42.68; H, 3.71; N, 25.16; S, 14.07.

Ethyl 5-(furan-2-yl)-1H-tetrazole-1-carboxylate **(22c)**: Yellow crystals (0.141 g, 68%), m.p. 109–110°C (acetonitrile). IR (KBr): 1725 (CO), 1630 (C=N), 1090 (C–O–C). ^{1}H NMR (DMSO-d_6) δ: 1.18 (t, 3H, CH_3, J = 7.24 Hz), 4.20 (q, 2H, OCH_2, J = 7.24 Hz), 7.18–7.93 (m, 3H, furan–H). ^{13}C NMR (DMSO-d_6) δ: 14.21 (CH_3), 62.52 (CH_2O), 125.87, 126.37, 141.93 (furan–CH), 153.74 (furan–C-2), 158.22 (C-5), 168.82 (CO). MS (*m/z*,%): 208 (M^+, 36), 163 (22), 135 (41), 93 (84), 67 (46), 45 (100). $C_8H_8N_4O_3$ (208.17): Calcd; C, 46.16; H, 3.87; N, 26.91. Found C, 45.95; H, 4.02; N, 27.13.

Ethyl 5-(pyridine-2-yl)-1H-tetrazole-1-carboxylate **(22d)**: Pale brown crystals (0.151 g, 69%), m.p. 136–138°C (ethanol). IR (KBr): 1730 (CO), 1625 (C=N), 1590 (ArC=C). ^{1}H NMR (DMSO-d_6) δ: 1.23 (t, 3H, CH_3, J = 7.18 Hz), 4.17 (q, 2H, OCH_2, J = 7.18 Hz), 7.31–8.34 (m, 4H, pyridine–H). ^{13}C NMR (DMSO-d_6) δ: 14.8 (CH_3), 62.78 (CH_2O), 126.64, 127.85, 132.12, 148.87 (pyridine–CH), 154.86 (pyridine–C-2), 158.21 (C-5), 168.74 (CO). MS (*m/z*,%): 219 (M^+, 39), 174 (52), 146 (16), 104 (100), 78 (162), 45 (86). $C_9H_9N_5O_2$ (219.20): Calcd; C, 49.31; H, 4.14; N, 31.95. Found C, 49.55; H, 3.98; N, 32.17.

Ethyl 5-(1H-indol-2-yl)-1H-tetrazole-1-carboxylate **(22e)**: Orange crystals (0.167 g, 65%), m.p. 174–176°C (methanol). IR (KBr): 3290 (NH), 1720 (CO), 1625 (C=N), 1590 (ArC=C). ^{1}H NMR (DMSO-d_6) δ: 1.25 (t, 3H, CH_3, J = 7.28 Hz), 4.18 (q, 2H, OCH_2, J = 7.28 Hz), 6.69 (s, 1H, indole–CH), 7.12–7.62 (m, 4H, ArH), 11.76 (br, 1H, indole–NH). ^{13}C NMR (DMSO-d_6) δ: 14.05 (CH_3), 62.55 (CH_2O), 101.16 (indole–CH), 126.87, 127.52 (ArCH), 131.16, 132.26, 133.34 (ArC and indole–C-2), 158.46 (C-5), 168.34 (CO). MS (*m/z*,%): 257 (M^+, 42), 212 (34), 184 (17), 142 (66), 91 (100), 77 (78), 65 (63), 45 (55). $C_{12}H_{11}N_5O_2$ (257.25): Calcd; C, 56.03; H, 4.31; N, 27.22. Found C, 55.87; H, 4.24; N, 27.46.

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