Regioselective Synthesis of Diazaspiro[4.4]nona- and Tetrazaspiro[4.5]deca-2,9-diene-6-one Derivatives

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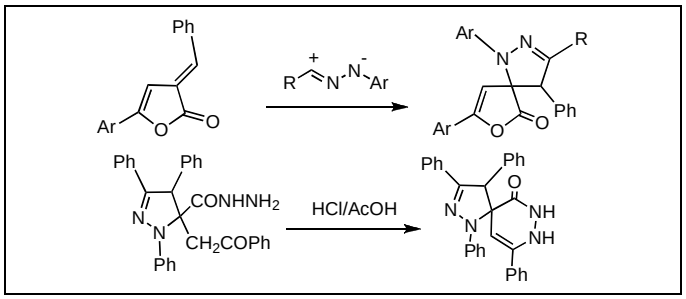

Several 1,2-diazaspiro[4,4]nona-2,8-diene-6-one derivatives were synthesised *via* cycloaddition of nitrilimides to 3-aryliden-2(3H)-furanone derivatives. The formed products react with hydrazine hydrate to give the corresponding pyrazolecarbohydrazide derivatives which undergo intramolecure cyclization upon treatment with HCl/AcOH mixture to afford 1,2,7,8-tetrazaspiro[4.5]deca-2,9-diene-6-one derivatives. Molecular mechanics energy minimization techniques and related structural parameters for compound 8-(4-methylphenyl)-1,3,4-triphenyl-7-oxa-1,2-diazaspiro[4.4]nona-2,8-diene-6-one **5a** are reported.

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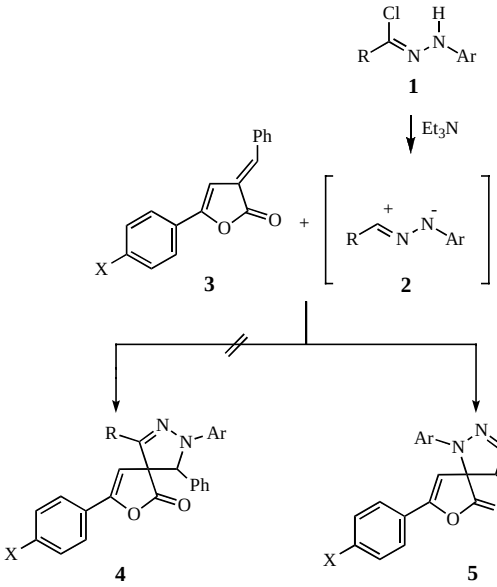
INTRODUCTION

The considerable pharmacological importance of furan-2-one derivatives have attracted a great deal of attention [1-6]. The various changes in the structure of these compounds are worth studying in order to synthesize less toxic and more potent drugs. Thus, attachment of other heterocyclic moieties, which are known to possess pharmacological activity, to furan ring may lead to the fulfillment of this objective. On the other hand, pyrazole derivative are known to have significant biological and pharmacological activity [7-9]. As an extension of our research program aiming at the synthesis of a variety of heterocyclic systems for biological screening [10-20], we report here on the syntheses of some important diazo-spiro[4.4]nona- and tetrazaspiro[4.5]deca-2,9-diene-6-one derivatives.

RESULTS AND DISCUSSION

In the course of our investigation, we have found that 3-phenylmethylene-5-arylfuran-2(3*H*)-ones **3**, are excellent building blocks for the synthesis of a variety spiropyr-azole ring systems [21-23]. Thus, treatment of 3-phenyl-methylene-5-arylfuran-2(3*H*)-ones **3** with nitrileimides **2a-i**) generated *in situ* by the action of triethylamine on hydrazonoyl chlorides **1a-i** [24-26]), in benzene under reflux, afforded the corresponding cycloadducts **5a-i** in good yields (Scheme 1). The reactions of **2** with **4** are regioselective and, in each case, only one regioisomer of **5** was isolated. This regioselectivity was evidenced from TLC and ^{1}H nmr analysis of the crude reaction product.

Scheme 1



4,5	X	R	Ar
a	CH_3	C_6H_5	C_6H_5
b	OCH_3	C_6H_5	C_6H_5
c	H	COOEt	C_6H_5
d	H	COOEt	4-$CH_3C_6H_4$
e	H	COOEt	4-ClC_6H_4
f	CH_3	COOEt	C_6H_5
g	CH_3	COOEt	4-$CH_3C_6H_4$
h	CH_3	COOEt	4-ClC_6H_4
i	H	CONHPh	C_6H_5

The ^{1}H nmr spectrum of compound **5a**, taken as a typical example of the prepared series, displayed a singlet signal at δ 2.15 due to methyl protons and showed two singlet signals in the region at δ 5.01 and 5.23 assigned to the CH protons of the pyrazole and furanone ring residues, respectively, in addition to a multiplet at δ 7.15-7.35 corresponding to the aromatic protons. Data produced using MM2 method *via* energy minimization techniques followed by molecular dynamics run for 20000 fs at room temperature, in the form of Cartesian coordinations for all representative atoms including H-atom (all atoms force field) are normaly representive of x, y, z, coordinates obtained from single crystal diffractions method [27-29].

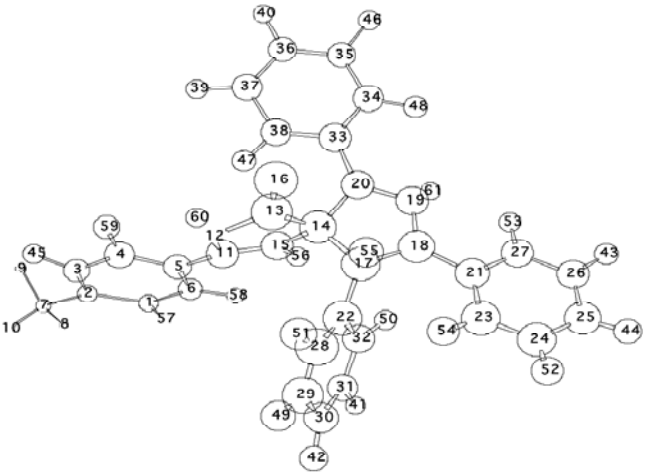
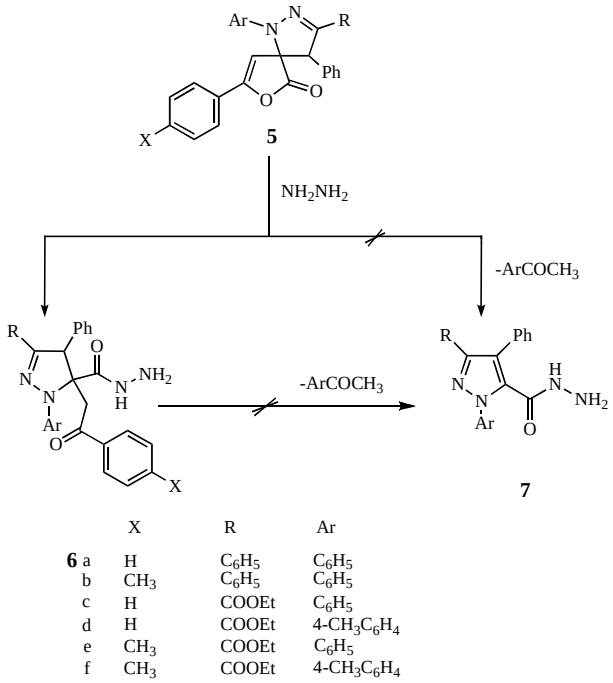


Figure 1. Molecular structure of **5a**

Treatment of the 7-oxa-1,2-diazaspiro[4.4]nona-2,8-diene-6-one derivatives **5a-f** with hydrazine hydrate, in ethanol at room temperature afforded the corresponding 1-aryl-4-phenyl-5-(2-Phenyl-2-oxoethyl)-pyrazole-5-carbohydrazide derivatives **6a,b** and ethyl 5-(hydrazinocarbonyl)-5-(2-phenyl-2-oxoethyl)-1,4-diphenyl-4,5-dihydro-1*H*-pyrazole-3-carboxylate derivatives **6c-f**, respectively (Scheme 2).

The structures of the isolated products were assigned on the basis of their elemental analyses and spectral data. For example, the ir spectra of compounds **6a,b** showed, in each case, two strong carbonyl absorption bands in the region 1710-1680 cm^{-1} and showed three bands in the region 3300-3430 cm^{-1} corresponding to NH and NH_2 groups. The ^{1}H nmr spectrum of compound **6b**, taken as a typical example of the prepared series, revealed two singlet signals at δ 2.15 and δ 4.16 corresponding to methyl and methylene protons, respectively, and two broad bands (D_2O-exchangeable) at δ 8.78 and 3.87 due to NH and NH_2 protons, respectively, in addition to multiplet signals in the region δ 7.25-7.50 due to aromatic protons. Moreover, the mass spectrum of compound **6a** revealed a peak at *m/z* 474 corresponding to its molecular ion.

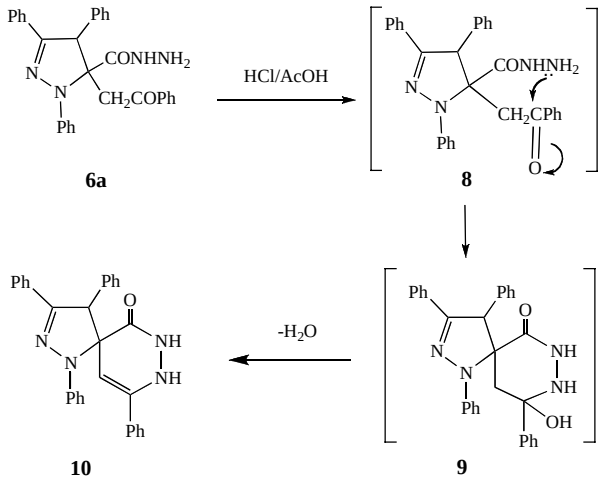
Scheme 2



	X	R	Ar
6 a	H	C_6H_5	C_6H_5
b	CH_3	C_6H_5	C_6H_5
c	H	COOEt	C_6H_5
d	H	COOEt	4-$CH_3C_6H_4$
e	CH_3	COOEt	C_6H_5
f	CH_3	COOEt	4-$CH_3C_6H_4$

Treatment of 5-(2-phenyl-2-oxoethyl)-1,3,4-triphenyl-4,5-dihydro-1*H*-pyrazole-5-carbohydrazide **6a** with a mixture of hydrochloric acid and glacial acetic acid at reflux temperature, afforded a single product (TLC) identified as 1,3,4,9-tetraphenyl-1,2,7,8-tetraza-spiro[4.5]-deca-2,9-diene-6-one **10** (Scheme 3). The IR spectrum of the isolated product **10** showed a band at 3417 cm^{-1} due to NH group and a strong absorption band at 1744 cm^{-1} due to carbonyl group. These results indicate that the reaction of **6a** with hydrochloric acid and glacial acetic acid proceeds, *via* the elimination of water molecule from the non-isolable intermediate **9**.

Scheme 3



EXPERIMENTAL

All melting points were measured on a Gallenkamp melting point apparatus and are uncorrected. The infrared spectra were recorded in potassium bromide disks on a Pye Unicam SP 3300 and Shimadzu FT ir 8101 PC infrared spectrophotometers. The nmr spectra were recorded on a Varian Mercury VX-300 nmr spectrometer. ^{1}H (300 MHz) and ^{13}C nmr (75.46 MHz) were run in deuterated chloroform ($CDCl_3$) or dimethylsulphoxide (DMSO-d_6). Chemical shifts were related to that of the solvent. Mass spectra were recorded on a Shimadzu GCMS-QP 1000 EX mass spectrometer at 70 e.V. Elemental analyses were carried out at the Microanalytical Center of Cairo University, Giza, Egypt.

8-Aryl-1,3,4-triphenyl-7-oxa-1,2-diazaspiro[4.4]nona-2,8-diene-6-one derivatives 5a,b. General procedure. To a solution of the appropriate arylidenefuranone derivative **3**)10 mmol) and *N*-phenylbenzohydrazonyl chloride **1a,b** (10 mmol), in dry benzene (30 mL), was added triethylamine (10 mmol) and the mixture was refluxed for 4 h then allowed to cool. The solid that formed was collected by filtration, washed with methanol and crystallization from ethanol.

8-(4-Methylphenyl)-1,3,4-triphenyl-7-oxa-1,2-diazaspiro-[4.4]nona-2,8-diene-6-one (5a). Yield 73%; mp 183-184 °C; ir (KBr) $\nu/_{max}$ cm^{-1} 1801 (C=O of lactone). ^{1}H nmr (δ, ppm, $CDCl_3$): 2.15 (s, 3H, CH_3), 5.01 (s, 1H, CH-pyrazole), 5.23 (s, 1H, CH-furanone), 7.15-7.35 (m, 19H, ArHs). *Anal.* Calcd for $C_{31}H_{24}O_2N_2$ (456.54): C, 81.55; H, 5.30; N, 6.14 Found: C, 81.70; H, 5.10; N, 6.00%.

8-(4-Methoxyphenyl)-1,3,4-triphenyl-7-oxa-1,2-diazaspiro-[4.4]nona-2,8-diene-6-one (5b). Yield 75%; mp 220-222 °C; ir (KBr) $\nu/_{max}$ cm^{-1} 1805 (C=O of lactone). ^{1}H nmr (δ, ppm, $CDCl_3$): 3.88 (s, 3H, OCH_3), 6.81 (s, 1H, CH-pyrazole), 6.99 (s, 1H, CH furanone), 7.13-7.35 (m, 19H, ArHs). ^{13}C nmr)δ, ppm, $CDCl_3$): 55.41, 97.69, 114.4, 120.73, 125.66, 127.04, 129.0, 129.8, 129.90, 133.8, 135.39. 156.97, 161.50. MS (*m/z*): 472 (M^+), 444, 194, 135, 91, 77. *Anal.* Calcd for $C_{31}H_{24}O_3N_2$ (472.54): C, 78.80; H, 5.12; N, 5.93%. Found: C, 79.00; H, 5.30, N, 6.10%.

Ethyl 6-oxo-1,8-Diaryl-4-phenyl-7-oxa-1,2-diazaspiro[4.4]-nona-2,8-diene-3-carboxylate (5c-h). General procedure. To a solution of the appropriate arylidenefuranone derivative **3** (5 mmol), and the corresponding hydrazonyl chloride **1c-e** (5 mmol), in dry benzene (20 mL) was added triethylamine (0.8 mL, 6 mmol) and the mixture was refluxed for 6 h, then allowed to cool. The solvent was removed under reduced pressure and solid that formed was collected by filtration, washed with methanol and finally recrystallized from ethanol.

Ethyl 6-oxo-1,4,8-triphenyl-7-oxa-1,2-diazaspiro[4.4]nona-2,8-diene-3-carboxylate (5c). Yield 83%; mp 105-106 °C; ir (KBr) $\nu/_{max}$ cm^{-1} 1809 (C=O of lactone), 1724 (C=O of ester) .^{1}H nmr (δ, ppm, $CDCl_3$): 1.21 (t, 3H, CH_3), 4.23 (q, 2H, CH_2), 4.96 (s, 1H, CH-pyrazole), 5.32 (s, 1H, CH-furanone), 7.15-7.48 (m, 15H, ArH's). *Anal.* Calcd for $C_{27}H_{22}N_2O_4$ (438.48): C, 73.96; H, 5.05; N, 6.39%. Found: C, 73.70; H, 5.20; N, 6.20%.

Ethyl 6-oxo-4,8-diphenyl-1-(4-methylphenyl)-7-oxa-1,2-diazaspiro[4.4]nona-2,8-diene-3-carboxylate (5d). Yield 70%; mp 115-116 °C; ir (KBr) $\nu/_{max}$ cm^{-1} 1805 (C=O of lactone), 1712 (C=O of ester). ^{1}H nmr (δ, ppm, $CDCl_3$): 1.20 (t, 3H, ester-CH_3), 2.47 (s, 3H, CH_3), 4.21(q, 2H, ester-CH_2), 4.92 (s,1H,CH-pyrazole), 5.30 (s, 1H, CH-furanone), 7.16-7.39 (m, 14H, ArH's); MS (*m/z*): 452 (M^+), 379, 360, 105, 77. *Anal.* Calcd for $C_{28}H_{24}N_2O_4$ (452.507): C, 74.32; H, 5.34; N, 6.19%. Found: C, 74.20; H, 5.50; N, 6.00%.

Ethyl 6-oxo-1-(4-chlorophenyl-4,8-diphenyl-7-oxa-1,2-diazaspiro[4.4]nona-2,8-diene-3-carboxylate (5e). Yield 70%; mp 123 °C; ir (KBr) $\nu/_{max}$ cm^{-1} 1807 (C=O of lactone), 1714 (C=O of ester). ^{1}H nmr (δ, ppm, $CDCl_3$): 1.21 (t, 3H, ester-CH_3), 4.22 (q, 2H, ester-CH_2), 4.93 (s, 1H, CH-pyrazole), 5.30 (s, 1H, CH-furanone), 7.15-7.41 (m, 14H, ArH's). *Anal.* Calcd for $C_{27}H_{21}N_2O_4Cl$ (472.925): C, 68.57; H, 4.47; N, 5.92; Cl, 7.50%. Found: C, 68.70; H, 4.30; N, 6.10; Cl, 7.40%.

Ethyl 6-oxo-1,4-diphenyl-8-(4-methylphenyl)-7-oxa-1,2-diazaspiro[4.4]nona-2,8-diene-3-carboxylate (5f). Yield 80%; mp 110 °C; ir (KBr) $\nu/_{max}$ cm^{-1} 1813 (C=O of lactone), 1728 (C=O of ester). ^{1}H nmr (δ, ppm, $CDCl_3$) 1.23 (t, 3H, ester-CH_3), 2.37 (s, 3H, CH_3), 4.24 (q, 2H, ester-CH_2), 4.95 (s, 1H, CH-pyrazole), 5.27 (s, 1H, CH furanone), 7.16-7.34 (m, 14H, ArHs). ^{13}C nmr)δ, ppm, $CDCl_3$): 14.06, 21.45, 61.29, 61.47, 99.68, 117.72, 123.91, 124.29, 125.34, 128.22, 128.37, 129.05, 129.16, 129.46, 129.59, 129.99, 134.66, 141.37, 141.96, 142.10, 154.61, 161.07,174.25. *Anal.* Calcd for $C_{28}H_{24}N_2O_4$ (452.507): C, 74.32; H, 5.34; N, 6.19%. Found: C, 74.10; H, 5.50; N, 6.30%.

Ethyl 6-oxo-1,8-di(4-methylphenyl)-4-phenyl-7-oxa-1,2-diazaspiro[4.4]nona-2,8-diene-3-carboxylate (5g). Yield 75%; mp 115 °C; ir (KBr) $\nu/_{max}$ cm^{-1} 1805 (C=O of lactone), 1728 (C=O of ester). ^{1}H nmr (δ, ppm, $CDCl_3$): 1.20 (t, 3H, ester-CH_3), 2.24 (s, 3H, CH_3), 2.41 (s, 3H, CH_3), 4.2 (q, 2H, ester-CH_2), 4.91 (s, 1H, CH pyrazole), 5.22 (s, 1H, CH furanone), 7.11-7.33 (m, 13H, ArHs). ^{13}C nmr)δ, ppm, $CDCl_3$): 14.03, 21.46, 61.40, 78.81, 99.01, 99.24, 119.01, 124.08, 125.31, 125.36, 128.19, 128.47, 129.11, 129.18, 129.22, 129.52, 129.59, 129.98, 130.04, 134.38,134.66, 140.67, 141.59, 154.88,154.91, 160.85, 173.94. *Anal.* Calcd for $C_{29}H_{26}N_2O_4$ (466.539): C, 74.66; H, 5.61; N, .6.00%. Found: C, 74.40; H, 5.70; N, 6.20%.

Ethyl 6-oxo-1-(4-chlorophenyl)-8-(4-methylphenyl)-4-phenyl-7-oxa-1,2-diazaspiro[4.4]nona-2,8-diene-3-carboxylate (5h). Yield 78%; mp 113 °C; ir (KBr) $\nu/_{max}$ cm^{-1} 1805 (C=O of lactone), 1732 (C=O of ester). ^{1}H nmr (δ, ppm, $CDCl_3$): 1.22 (t, 3H, ester-CH_3), 2.37 (s, 3H, CH_3), 4.23 (q, 2H, ester-CH_2), 4.94 (s, 1H, CH- pyrazole), 5.25 (s, 1H, CH-furanone), 7.17-7.34 (m, 13H, ArHs). ^{13}C nmr (δ, ppm, $CDCl_3$): 14.03, 21.46, 61.42, 61.48, 99.00,99.24, 119.01, 124.08, 125.31, 125.36, 128.19, 128.47, 129.03, 129.11, 129.18, 129.22, 129.52, 129.59, 129.98, 130.04, 134.38, 134.66, 140.67, 141.59, 142.88, 154.91, 160.85, 173.94. MS (*m/z*): 488 (M+2), 486 (M^+), 458, 262, 119, 91, 77. *Anal* Calcd.for $C_{28}H_{23}N_2O_4Cl$ (486.95): C, 69.06; H, 4.76; N, 5.75; Cl, 7.28%. Found: C, 69.13; H, 4.85; N, 5.82; Cl, 7.52%.

6-Oxo-*N*,1,4,8-tetraphenyl-7-oxa-1,2-diazaspiro[4.4]nona-2,8-diene-3-carboxamide (5i). To a solution of the benzylidene-furanone **3a** (3 mmol) and the hydrazonyl chloride **1i** (3 mmol) in dry benzene (20 mL) was added triethylamine (3 mmol) and the mixture was refluxed for 4 h. The solvent was removed under reduced pressure and the solid that formed was collected washed with methanol and recrystallization from ethanol. Yield 78%; mp 180 °C; ir (KBr) $\nu/_{max}$ cm^{-1} 3394 (NH), 1850 (C=O of lactone), 1681 carbonyl of (CO-NHPh). MS (*m/z*) 485 (M^+), 457, 363, 335, 259, 231, 105, 77. ^{1}H nmr (δ, ppm, $CDCl_3$): 5.05 (s, 1H, CH-pyrazole), 5.33 (s, 1H, CH furanone), 7.25-7.45 (m, 20H, ArHs), 8.5 (s, 1H, NH). *Anal.* Calcd for $C_{31}H_{23}N_3O_3$ (485.540). C, 76.68; H, 4.77; N, 8.65%. Found: C, 76.9; H, 4.50; N, 8.30%.

Synthesis of 5-(2-Phenyl-2-oxoethyl)-1,3,4-triphenyl-4,5-dihydro-1*H*-pyrazole 5-carbohydrazide and Ethyl 5-(hydrazinocarbonyl)-5-[2-phenyl-2-oxoethyl]-1,4-diphenyl-4,5-dihydro-1*H*-pyrazole-3-carboxylate derivatives 6a,b and 6c-f. General Procedure. Hydrazine hydrate (80%, 2 mL) was added to a stirred solution of the appropriate spiropyrazolofuranone derivatives **5a-f** (0.5 gm) in absolute ethanol (20 mL) and the reaction mixture was stirred for 4 hours. The color of spiropyrazolofuranone derivative disappears and white precipitate was formed. The precipitated solid was collected by filtration, washed with ethanol and crystalized from absolute ethanol.

5-(2-Phenyl-2-oxoethyl)-1,3,4-triphenyl-4,5-dihydro-1*H*-pyrazole-5-carbohydrazide (6a). Yield 80%; mp 175 °C; ir (KBr) $\nu/_{max}$ cm^{-1} 3300-3430 (NH, NH_2), 1710, 1680 (2 C=O); ^1H nmr (δ, ppm,$CDCl_3$): 8.76 (s, 1H, NH), 3.75 (s, 2H, NH_2), 4.15 (s, 2H, CH_2), 4.83 (s, 1H, CH pyrazole), 7.25-7.51 (m, 20H, ArHs). MS (*m/z*): 474 (M^+), 456, 415, 336, 309, 194, 130, 91, 77, 51. *Anal*. Calcd for $C_{30}H_{26}N_4O_2$ (474.559): C, 75.92; H, 5.47; N, 11.80%**.** Found: C, 76.30; H, 5.70; N, 11.90%**.**

5-[2-(4-Methylphenyl)-2-oxoethyl]-1,3,4-triphenyl-4,5-dihydro-1*H*-pyrazole-5-carbohydrazide (6b). Yield 82%; mp.130 °C; ir (KBr) $\nu/_{max}$ cm^{-1} 3300-3430 (NH, NH_2), 1710 (C=O), 1680 (C=O). ^1H nmr (δ, ppm, $CDCl_3$): 2.15 (s, 3H, CH_3), 8.78 (s, 1H, NH), 3.78 (s, 2H, NH_2), 4.16 (s, 2H, CH_2), 4.84 (s, 1H, CH pyrazole), 7.25-7.50 (m, 19H, ArHs). *Anal*. Calcd for $C_{31}H_{28}N_4O_2$ (488.58): C, 76.20; H, 5.77; N, 11.46%**.** Found: C, 76.60; H, 6.00; N, 11.60%**.**

Ethyl 5-(hydrazinocarbonyl)-5-[2-phenyl-2-oxoethyl]-1,4-diphenyl-4,5-dihydro-1*H*-pyrazole-3-carboxylate (6c). Yield 70%; mp 128 °C; ir (KBr) $\nu/_{max}$ cm^{-1} 3394, 3317 (NH, NH_2), 1712, 1689 (2 C=O); ^1H nmr (δ, ppm, $CDCl_3$): 1.13 (s, 3H, ester-CH_3), 2.67 (s, 2H, CH_2), 2.74 (s, 1H, NH), 3.64 (s, 1H, CH-pyrazole), 3.87 (s, 2H, NH_2), 4.12 (q, 2H, ester-CH_2), 7.25-7.41 (m, 15H, ArHs). MS (*m/z*): 470 (M^+), 452, 411, 390, 365, 233, 130, 105, 77, 51. ^{13}C nmr (δ, ppm, $CDCl_3$): 13.91, 39.79, 58.10, 60.59, 75.26, 89.27, 119.72, 122.09, 124.09, 125.10, 127.87,128.25, 128.37, 128.59, 128.84,128.90, 129.17, 129.30, 129.65, 131.86, 134.49, 140.95, 141.92, 141.97, 161.66, 170.63. *Anal*. Calcd for $C_{27}H_{26}N_4O_4$ (470.52): C, 68.92; H, 5.57; N, 11.90%**.** Found: C, 69.10; H, 6.01 N, 12.00%**.**

Ethyl 5-(hydrazinocarbonyl)-5-[2-phenyl)-2-oxoethyl]-1(4-methylphenyl)-4-phenyl-1*H*-pyrazole-3-carboxylate (6d). Yield 75%; mp 160 °C; ir (KBr) $\nu/_{max}$ cm^{-1} 3355, 3300 (NH, NH_2), 1712, 1687 (2C=O). ^1H nmr (δ, ppm, $CDCl_3$): 1.15 (t, 3H, ester-CH_3), 2.74 (s, br, 1H, NH), 2.54 (s, 3H, CH_3), 3.87 (s, 2H, NH_2),4.16 (s, 2H, CH_2), 4.18 (q, 2H, ester-CH_2), 4.94 (s, br, 1H, CH-pyrazole), 7.17-7.29 (m, 14H, ArHs). *Anal*. Calcd for $C_{28}H_{28}N_4O_4$ (484.55).: C, 69.40; H, 5.82; N, 11.56%**.** Found: C, 69.80; H, 6.10; N, 11.80%**.**

Ethyl 5-(hydrazinocarbonyl)-5-[2-(4-methylphenyl)-2-oxoethyl]-1,4-diphenyl-1*H*-pyrazole-3-carboxylate (6e). Yield 83%; mp 198 °C; ir (KBr) $\nu/_{max}$ cm^{-1} 3327, 3276 (NH, NH_2), 1718, 1697 (2C=O). ^1H nmr (δ, ppm, $CDCl_3$): 1.14 (t, 3H, ester-CH_3), 2.32 (s, br, 1H, NH), 2.62 (s, 3H, CH_3), 3.87 (s, 2H, NH_2), 4.13 (s, 2H, CH_2), 4.18 (q, 2H, ester-CH_2), 4.80 (s, br., 1H, CH-pyrazole), 7.17-7.38 (m, 14H, ArHs). ^{13}C nmr (δ, ppm, $CDCl_3$): 13.94, 20.92, 39.89, 59.47, 60.94, 89.12, 120.10, 124.31, 124.98, 127.90, 128.62, 129.11, 129.21, 129.28, 134.52, 138.28, 13880, 141.06, 142.00, 161.63, 170.46. *Anal*. Calcd for $C_{28}H_{28}N_4O_4$ (484.55): C, 69.40; H, 5.82; N, 11.56%**.** Found: C, 69.70; H, 5.60; N, 11.70%**.**

Ethyl 5-(hydrazinocarbonyl)-5-[2-(4-methylphenyl)-2-oxoethyl]-1-(4-methylphenyl)-1-phenyl-1,4-dihydropyrazole-3-carboxylate (6f). Yield 85%; mp 120 °C; ir (KBr) $\nu/_{max}$ cm^{-1} 3494, 3352 (NH, NH_2), 1705, 1689 (2C=O); ^1H nmr (δ, ppm, $CDCl_3$): 1.15 (t, 3H, ester-CH_3), 2.29 (s, 6H, $2CH_3$), 2.74 (s, 1H, NH), 3.87 (s, 2H, NH_2), 4.16 (s, 2H, CH_2), 4.18 (q, 2H, ester-CH_2), 4.84 (s, 1H, CH pyrazole), 6.9-7.82 (m, 13H, ArHs). *Anal*. Calcd for $C_{29}H_{30}N_4O_4$ (498.62): C, 69.86; H, 6.01; N, 11.23%. Found: C, 70.10; H, 6.21; N, 11.40 %.

Cyclization of 5-(2-Phenyl-2-oxoethyl)-1,3,4-triphenyl-4,5-dihydro-1*H*-pyrazole-5-carbohydrazide. Synthesis of 1,3,4,9-tetraphenyl-1,2,7,8-tetrazaspiro[4.5]deca-2,9-diene-6-one (10). A mixture of glacial acetic acid (5 mL), hydrochloric acid (34%, 10 mL) and pyrazole-5-carbohydrazide **6a** (20 mmol) was refluxed for 5 hour. The reaction mixture was allowed to cool and poured into ice-cold water. The precipitated solid was collected by filtration, washed with water and crystallized from ethanol. Yield 50%; mp 158 °C; ir (KBr) $\nu/_{max}$ cm^{-1} 3417 (NH), 1744 (C=O); ^1H nmr (δ, ppm, DMSO-d_6): 3.46 (s, 1H, CH-pyridazine), 5.80 (s, 1H, CH-pyrazole), 7.31-7.88 (m, 20H, ArHs), 8.66 (s, 1H, NH), 12.23 (s, 1H, NH). *Anal*. Calcd for $C_{30}H_{24}N_4O$ (456.54): C, 78.92; H, 5.30; N, 12.27%. Found: C, 79.10; H, 4.90; N, 12.53%. ^{13}C nmr (δ, ppm, DMSO-d_6): 47.81, 70.54, 95.62, 114.83, 115.18, 116.31, 122.12, 125.07, 126.81, 126.93, 127.09, 127.34, 127.65, 128.07, 128.26, 128.50, 128.72, 128.86, 129.26, 129.56, 129.88, 131.97, 132.69, 133.77, 135.85, 136.97, 137.65, 142.41, 148.52, 177.88.

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