Synthesis and Some Reactions of 4-(Ethoxycarbonyl)-1,5-Diphenyl-1*H*-pyrazole-3-carboxylic Acid

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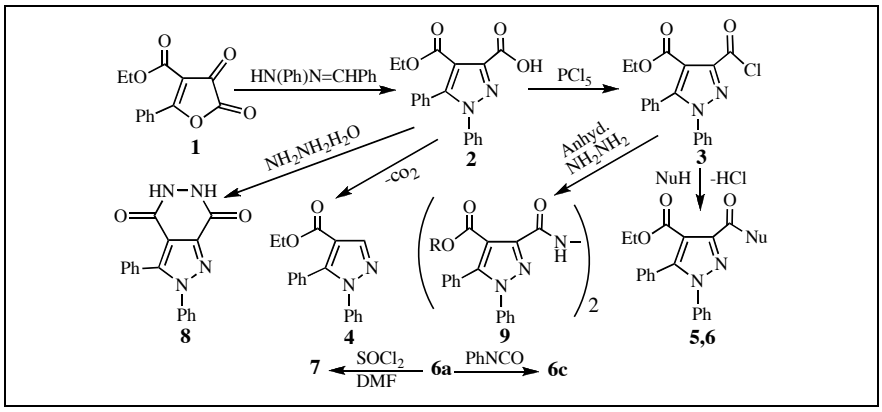

1,5-Diphenyl-1*H*-pyrazole-3,4-dicarboxylic acid-4-ethyl ester **2**, obtained from the 4-ethoxycarbonyl-5-phenyl-2,3-furandione **1** and *N*-benzylidene-*N*'-phenyl hydrazine, was converted *via* reactions of its acid chloride **3** with various alcohols or N-nucleophiles into the corresponding ester **5** or amide derivatives **6**, respectively. In addition, **2** was decarboxylated to give ethyl 1,5-diphenylpyrazole-4-carboxylate **4**. Nitrile **7** derivative of **2** was also obtained by dehydration of **6a** in a mixture of $SOCl_2$ and DMF. While cyclocondensation reaction of **2** with hydrazine hydrate leads to the formation of pyrazolo[3,4-*d*]pyridazine-4,7-dione **8**, the reaction of **3** with anhydrous hydrazine provided a new bis pyrazole derivative **9**.

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INTRODUCTION

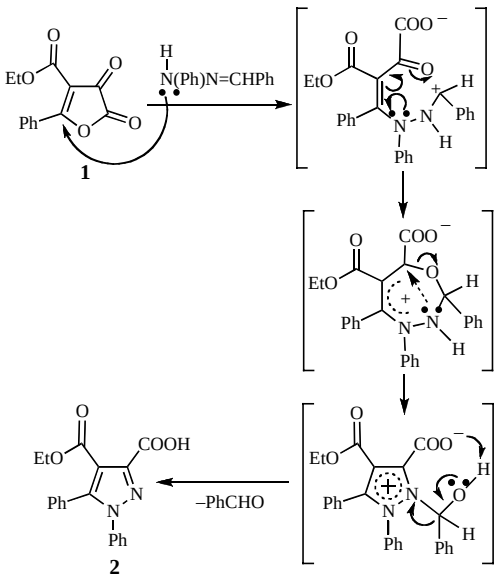
Furandiones are extremely versatile synthons in heterocyclic chemistry [1]. Thermal decarbonylation of these compounds yields α-oxoketenes as an intermediate which are capable of undergoing cyclo- and nucleophilic addition reactions with heterodienophiles and nucleophiles, respectively [2]. In addition, these compounds also show typical carbonyl, lacton and α,β-unsaturated carbonyl reactions depending on the structures of the nucleophiles [3]. On the other hand, furandiones, depending on functionalities at particularly C-4 position, can exhibit different behaviors towards nucleophiles as well as cycloaddition processes [4]. A literature survey revealed that, so far, only 4-aroyl-furandiones have been reacted with hydrazines or hydrazones affording the corresponding 1*H*-pyrazole-3-carboxylic acids [3b,3d,3e,3g,3h,4e], various analogues of which proved to be interesting in a chemical and biological context due to showing pharmacological action with a wide spectrum [5]. In an attempt to help remedy this situation we decided to extend our previous studies [3a,3b,3d,3e,4e,6] on the reactions of a different furandione **1**, bearing ester group at C-4 position, with hydrazones. Our approach was achieved by synthesis of a new 1*H*-pyrazole derivative **2** with *ortho* functional groups capable of forming the pyridazine ring.

RESULTS AND DISCUSSION

Without any solvent, heating of furandione **1** and phenyl hydrazone of benzaldehyde (1/1 mole) for about 1 h. led to the formation of pyrazole-3,4-dicarboxylic acid derivative **2**, which was also recently synthesized by a different method [7], in approximately 30 % yield. The moderate yield of the reaction can be explained by the chemical behavior of furandione **1** towards H-active nucleophiles. Carbon atoms C-2, C-3 and C-5 in furandiones are electrophilic sites having different reactivity and could be used for the construction reactions with nucleophiles [8]. Simultaneous attacks of H-active nucleophiles to both C-2 and C-3 positions of the furan ring could convert furandiones into starting materials; these materials are dibenzoylmethane and oxalic acid derivatives [9]. The by-products formed in this way are removed when the raw product is treated with diethyl ether. A reasonable proposal similar to that discussed with 4-benzoyl-5-phenyl-2,3-furandione [3d] for reaction

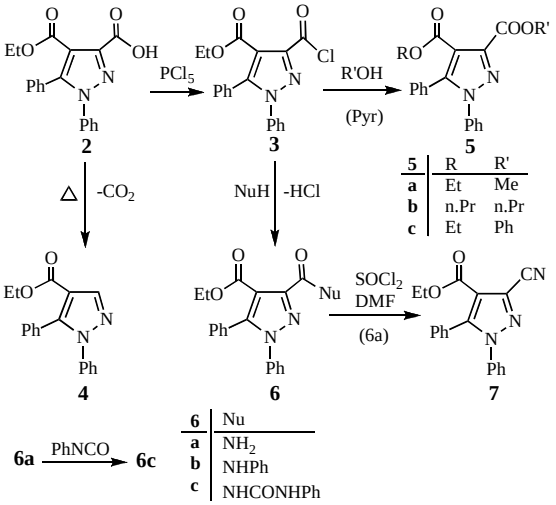
pathway from furandione **1** to pyrazole acid **2** is outlined briefly in Scheme 1.

Scheme 1



Structure of compound **2** was confirmed by analytical and spectral data (see Experimental). In addition, the acid **2** could be converted into the corresponding acid chloride **3**, decarboxylation product **4** that is previously known [10], ester **5**, amide **6** and nitrile **7** derivatives by the usual chemical procedures (Scheme 2). While 4-benzoyl pyrazole-3-carboxylic acids could be easily converted by $SOCl_2$ into the corresponding acid chloride [3b,3d,3e,6], conversion of **2** with only PCl_5, and with difficulty, into the corresponding acid chloride **3** may be referred to a steric effect (*ortho*-effect) originated from ethyl carboxylate side chain at C-4 position of **2**. On the otherhand, while esterification reaction between chlorocarbonyl group of **3** and methanol did not lead to any simultaneous different reaction with the ester group of **3**, the occurring of trans-esterification on the ethyl carboxylate side chain at C-4 position of **3** during the esterification reaction between chlorocarbonyl group of **3** and propanol is interesting. This may be due to the volatility differences between methanol, ethanol and propanol (Scheme 2).

Scheme 2



5	R	R'
a	Et	Me
b	n.Pr	n.Pr
c	Et	Ph

6	Nu
a	NH_2
b	NHPh
c	NHCONHPh

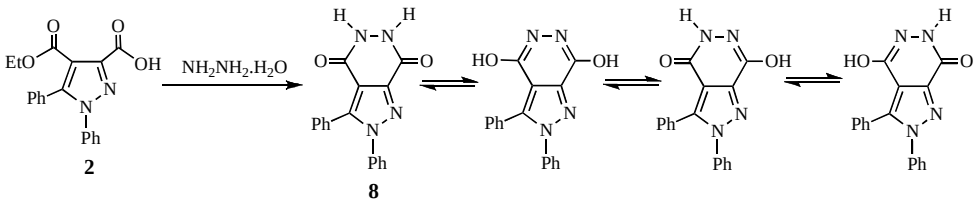
The correct structure of the unsymmetrically substituted urea derivative was established by another chemical procedure consisting of the reaction of primary amide **6a** with phenylisocyanate which resulted in formation of phenylurea derivative **6c**, originally prepared from the acid chloride **3** in the usual way.

Reaction of pyrazole derivatives having functionalities such as carbonyls, esters, carboxylic acids and nitriles in the *ortho*-positions according to each other with hydrazines may be a convenient method to build the pyrazolo[3,4-*d*]pyridazine system [11]. Thus, the pyrazole acid **2** was cyclized with hydrazine hydrate to a pyrazolo[3,4-*d*]pyridazinedione derivative **8**, both itself and its tautomeric structures of which are previously known [12], in approximately 38% yield (Scheme 3).

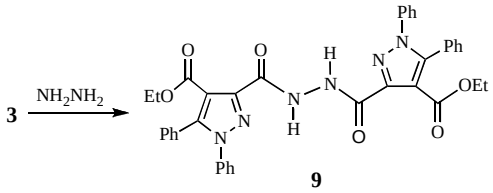
As mentioned above, while cyclocondensation reaction of pyrazole acid **2** with excess hydrazine hydrate gives pyrazolo-pyridazine derivative **8**, the reaction of its acid chloride **3** with anhydrous hydrazine at room temperature led to the formation of a novel bis pyrazole compound **9** (Scheme 4).

Both undergoing ring closure reaction of **2** with only excess hydrazine hydrate for giving pyrazolo[3,4-*d*]-pyridazine system **8** and forming of bis-pyrazole derivative **9** during the equimolar reaction of **3** with anhydrous hydrazine may be an indication of pronounced tendency to form open chain poly-condensation products of 1*H*-pyrazole-3,4-dicarboxylic acid derivatives with hydrazines.

Scheme 3



Scheme 4



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The structures of all these pyrazole derivatives, obtained from **3**, were confirmed by analytical, IR, ^{1}H-nmr and ^{13}C nmr spectroscopic data, based on the structural analogy of similar compounds [3a-e, 4e,6,10, 12,13] (see Experimental).

EXPERIMENTAL

Solvents were dried by refluxing with the appropriate drying agents and distilled before use. Melting points were determined on an Electrothermal Gallenkamp apparatus and are uncorrected. Microanalyses were performed on a Carlo Erba Elemental Analyzer Model 1108.The ir spectra were obtained as potassium bromide pellets using a Mattson 1000 FTIR spectrometer. The ^{1}H and ^{13}C nmr spectra were recorded on Varian XL-200 (200 MHz) and Varian XL-200 (50 MHz) spectrometers, respectively, using TMS as an internal standard. All experiments were followed by using DC Alufolien Kieselgel 60 F 254 Merck and Camag tlc lamp (254/366 nm)

4-(Ethoxycarbonyl)-1,5-Diphenyl-1*H*-pyrazole-3-carboxylic acid (2). An equimolar mixture of **1** (0.246 g, 1 mmol) and *N*-benzylidene-*N'*-phenyl hydrazine (0.196 g, 1 mmol) was heated to 90-100°C for approximately 40 min, without any solvent. After cooling to room temperature, the residue was treated with ether and the formed crude product was crystallized from a mixture of toluene and cyclohexane (volume ratio:1:1) to give 0.101 g (30 %) of **2,** mp 173°C; IR: 3250-2400 cm^{-1} (b, OH, COOH), 3065 cm^{-1} (Ar-H), 2977 cm^{-1} (R-H), 1738 cm^{-1} (C=O), 1642 cm^{-1} (C=O); ^{1}H nmr ($CDCl_3$): δ = 13.6 (br, H, COOH), 7.35-7.15 (m, 10H, Ar-H), 4.12 (q, *J* = 7.1 Hz, 2H, OCH_2), 0.88 ppm (t, *J* = 7.1 Hz, 3H, CH_3); ^{13}C nmr ($CDCl_3$): δ= 168.95 (C=O, COOH or ester), 162.05 (C=O, COOH or ester), 150.38 (N-Ph), 146,26 (C-3), 140.25 (C-5), 132.20, 131.61, 130.88, 130.76, 130.66, 130.13, 127.73, 113.86 (C-4), 64.66 (OCH_2), 15.16 ppm (CH_3). *Anal.* Calcd. for $C_{19}H_{16}N_2O_4$: C, 67.85; H, 4.79; N, 8.33. Found: C, 67.74; H, 4.78; N, 8.34.

3-Cholorocarbonyl-1,5-diphenyl-1*H*-pyrazole-4-carboxylic acid ethyl ester (3). **2** (0.336 g, 1mmol) and PCl_5 (0.208 g, 1 mmol) in CCl_4 were refluxed for 3 h. After the solvent was removed by evaporation, the oily residue was treated with dry ether and the formed crude product was crystallized cyclohexane. The yield 0.142 g (40 %) mp 97 °C; IR: 3090 cm^{-1} (Ar-H), 2984 cm^{-1} (R-H), 1726 cm^{-1} (C=O); ^{1}H nmr ($CDCl_3$): δ = 7.37-7.23 (m, 10H, Ar-H), 4.22 (q, *J* = 7.2 Hz, 2H, OCH_2), 1.19 ppm (t, *J* = 7.1 Hz, 3H, CH_3); ^{13}C nmr ($CDCl_3$): δ = 164.07 (C=O), 163.48 (C=O), 148.11 (N-Ph), 146.65 (C-3), 140.35 (C-5), 132.08, 131.86, 131.19, 131.10, 130.47, 129.29, 127.50, 118.32 (C-4), 63.63 (OCH_2), 15.77 ppm (CH_3). *Anal.*Calcd. for $C_{19}H_{15}ClN_2O_3$: C, 64.32; H, 4.26; CI, 9.99; N, 7.90. Found: C, 64.30; H, 4.26; CI, 10.00; N, 7.89.

1,5-Diphenyl-1*H*-pyrazole-4-carboxylic acid ethyl ester (4). Compound **2** (0.336 g, 1 mmol) was heated to 235-240°C on an oil bath for about 30 min, without any solvent. After cooling to room temperature, the residue was treated with ether to give crude product, which was then recrystallized from ethyl alcohol to yield 0.146 g (50 %) of **4**, identical in ir spectrum with literature compound mp 120°C (Reference [10a], mp 113°C; reference [10b], mp 112.5-114°C; reference [10c], mp 116°C; reference [10d], mp 116-118°C). ^{1}H nmr ($CDCl_3$): δ = 8.19 (s, 1H, H-3), 7.38-7.17 (m, 10H, Ar-H), 4.20 (q, *J* = 7.1 Hz, 2H, OCH_2), 1.22 ppm (t, *J* = 7.2 Hz, 3H, CH_3); ^{13}C nmr ($CDCl_3$): δ = 164.94 (C=O), 147.40 (N-Ph), 144.42 (C-3), 141.28 (C-5), 132.51, 131.06, 130.95, 130.80, 129.96, 129.86, 127.30, 115.93 (C-4), 62.05 (OCH_2), 16.15 ppm (CH_3). *Anal.* Calcd. for $C_{18}H_{16}N_2O_2$: C, 73.95; H, 5.52; N. 9.58. Found: C, 73.90; H, 5.51; N, 9.59.

1,5-Diphenyl-1*H*-pyrazole-3,4-dicarboxylic acid-4-ethyl-3-methyl ester (5a).

General Procedure. The acid chloride **3** (0.355 g, 1 mmol) and a moderate excess of methanol were refluxed together with a catalytic amount of pyridine for 3 h. After cooling, the solution was acidified by adding diluted hydrochloric acid (12 %) to give a crude solid that was crystallized from the same alcohol. The yield 0.263 g, (75 %), mp 95 °C ; IR: 3018 cm^{-1} (Ar-H), 2990 cm^{-1} (R-H), 1736 cm^{-1} (C=O); ^{1}H nmr ($CDCl_3$): δ = 7.33-7.27 (m, 10H, Ar-H), 4.21 (q, *J* = 7.1 Hz, 2H, OCH2), 3.97 (s, 3H, OCH_3), 1.17 ppm (t, *J* = 7.1 Hz, 3H, CH_3); ^{13}C nmr ($CDCl_3$): δ = 164.81 (C=O), 164.38 (C=O), 146.82 (N-Ph), 145.36 (C-3), 140.68 (C-5), 132.12, 131.41, 130.92, 130.53, 130.26, 130.01, 127.59, 117.78 (C-4), 63.10 (OCH_2), 54.49 (OCH_3), 15.87 ppm (CH_3). *Anal.*Calcd. for $C_{20}H_{18}N_2O_4$: C, 68.56; H, 5.18; N. 7.99. Found: C, 68.52; H, 5.19; N, 7.98.

1,5-Diphenyl-1*H*-pyrazole-3,4-dicarboxylic acid di-*n*-propyl ester (5b). Compound **5b** was prepared according to the general procedure with a reflux time 2.5 h. using 1-propanol as solvent, resulting in a 45 % yield (0.176 g), mp 130°C; IR: 3080 cm^{-1} (Ar-H), 2978 cm^{-1} (R-H), 1753 cm^{-1} (C=O); ^{1}H nmr ($CDCl_3$): δ = 7.36-7.19 (m, 10H, Ar-H), 4.35 (t, *J* = 6.8 Hz, 2H, OCH_2), 4.11 (t, *J* = 6.6 Hz, 2H, OCH_2), 1.81 (m, *J* = 7.1 Hz, 2H, CH_2), 1.55 (m, *J* = 7.0 Hz, 2H, CH_2), 1.01 (t, *J* = 7.4 Hz, 3H, CH_3), 0.79 ppm (t, *J* = 7.4 Hz, 3H, CH_3); ^{13}C nmr ($CDCl_3$): δ = 164.98 (C=O), 164.30 (C=O), 146.66 (N-Ph), 145.97 (C-3), 140.75 (C-5), 132.11, 131.36, 130.87 (2 C), 130.43, 130.26, 127.59, 117.49 (C-4), 69.24 (OCH_2), 68.74 (OCH_2), 23.99 (CH_2), 23.75 (CH_2), 12.36 (CH_3), 12.26 ppm (CH_3). *Anal.*Calcd. for $C_{23}H_{24}N_2O_4$: C, 70.39; H, 6.16; N. 7.14. Found: C, 70.36; H, 6.17; N, 7.15.

1,5-Diphenyl-1*H*-pyrazole-3,4-dicarboxylic acid-4-ethyl-3-phenylester (5c). The acid chloride **3** (0.355 g, 1 mmol) and phenol (0.094 g, 1 mmol) were refluxed together with a catalytic amount of pyridine in toluene for 7 h. After evaporation of the solvent, the oily residue was dissolved in ethyl alcohol then the solution was acidified by adding diluted hydrochloric acid (12 %) to give a crude solid, which was crystallized from ethanol. The yield 0.185 g (45 %), mp 120°C; IR; 3050 cm^{-1} (Ar-H), 2927 cm^{-1} (R-H), 1778 cm^{-1} (C=O), 1727 cm^{-1} (C=O); ^{1}H nmr ($CDCl_3$): δ = 7.47-7.23 (m, 15H, Ar-H), 4.25 (q, *J* = 7.1 Hz, 2H, OCH_2), 1.17 ppm (t, *J* = 7.1 Hz, 3H, CH_3); ^{13}C nmr ($CDCl_3$): δ = 164.49 (C=O), 162.39 (C=O), 152.68 (O-Ph), 146.98 (N-Ph), 144.94 (C-3), 140.70 (C-5), 132.17, 131.53, 131.46, 131.01, 130.67, 130.34, 129.97, 128.06, 127.63, 123.64, 118.30 (C-4), 63.28 (OCH_2), 15.93 ppm (CH_3). *Anal.*Calcd. for $C_{25}H_{20}N_2O_4$: C, 72.80; H, 4.89; N. 6.79. Found: C, 72.77; H, 4.89; N, 6.80.

3-Carbamoyl-1,5-diphenyl-1*H*-pyrazole-4-carboxylic acid ethyl ester (6a).

General Procedure. To the cold solution of acid chloride **3** (0.355 g, 1 mmol) in chloroform was added aqueous ammonia (0.15 mL, 2 mmol) at 0-5°C, with stirring and the stirring continued for 30 min. The formed white precipitate was isolated by filtration and recrystallized from methanol to give 0.257 g (59 %) of **6a**, mp 167°C; IR: 3464, 3336 cm^{-1} (NH_2), 3055 cm^{-1} (Ar-H), 2944 cm^{-1} (R-H), 1702 cm^{-1} (C=O), 1625 cm^{-1} (C=O, amide); ^{1}H nmr ($CDCl_3$): δ = 8.52 (br, 1H, NH), 7.37-7.19 (m, 10H, Ar-H), 6.20 (br, 1H, NH), 4.14 (q, *J* = 7.1 Hz, 2H, OCH_2), 0.98 ppm (t, *J* = 7.1 Hz, 3H, CH_3); ^{13}C nmr ($CDCl_3$): δ = 166.44 (C=O), 164.47 (C=O), 148.53 (N-Ph), 147.62 (C-3), 140.67 (C-5), 132.10, 131.24, 131.10, 130.80, 130.50, 130.15, 127.68, 115.50 (C-4), 63.28 (OCH_2), 15.48 ppm (CH_3). *Anal*. Calcd. for $C_{19}H_{17}N_3O_3$: C, 68.05; H, 5.11; N. 12.53. Found: C, 68.09; H, 5.10; N, 12.52.

1,5-Diphenyl-3-phenylcarbamoyl-1*H*-pyrazole-4-carboxylic acid ethyl ester (6b). Compound **6b** was prepared according to the general procedure using aniline as reagent, resulting in 57 % yield (0.234 g) mp 200 °C; IR: 3285 cm^{-1} (N-H), 3080 cm^{-1} (Ar-H), 2945 cm^{-1} (R-H), 1705 cm^{-1} (C=O), 1628 cm^{-1} (C=O); ^{1}H nmr ($CDCl_3$): δ = 10.60 (br, 1H, N-H), 7.82-7.12 (m, 15H, Ar-H), 4.18 (q, *J* = 7.1 Hz, 2H, OCH_2), 1.01 ppm (t, *J* = 7.1 Hz, 3H, CH_2); ^{13}C nmr ($CDCl_3$): δ = 166.87 (C=O), 160.28 (C=O), 148.60 (N-Ph), 148.47 (N-Ph), 140.68 (C-3), 140.30 (C-5), 132.08, 131.31, 131.04, 130.94, 130.86, 130.57, 130.21 127.68, 126.14, 122.09, 116.47 (C-4), 63.51 (OCH_2), 15.54 ppm (CH_3). *Anal*.Calcd. for $C_{25}H_{21}N_3O_3$: C, 72.98; H, 5.14; N. 10.21. Found: C, 72.94; H, 5.15; N, 10.22.

1,5-Diphenyl-3-(3-phenylüreidocarbonyl)-1*H*-pyrazole-4-carboxylic acid ethyl ester (6c).

Method A: From Acid Chloride 3. An equimolar mixture of the acid chloride **3** (0.355 g, 1 mmol) and phenyl-urea (0.136 g, 1 mmol) was refluxed in xylene for 4 h. After evaporation of the solvent, the oily residue was treated with ether and the formed crude product was recrystallized from methanol. The yield 0.182 g (40 %), mp 165°C ; IR: 3387 cm^{-1} (NH), 3080 cm^{-1} (Ar-H), 2953 cm^{-1} (R-H), 1753 cm^{-1} (C=O), 1651 cm^{-1} (C=O); ^{1}H nmr ($CDCl_3$): δ = 7.93 (br, NH), 7.44-6.90 (m, 15H, Ar-H), 4.18 (q, *J* = 7.2 Hz, 2H, OCH_2), 0.95 ppm (t, *J* = 7.2 Hz, 3H, CH_3); ^{13}C nmr ($CDCl_3$), δ = 169.07 (C=O), 162.41 (C=O), 150.43 (C=O), 146.32 (N-Ph), 143.89 (C-3), 141.24 (C-5), 140.14 (N-Ph), 132.21, 131.70, 130.99, 130.86, 130.70, 130.64, 130.20, 127.71, 124.54, 121.64, 113.83 (C-4), 64.79 (OCH_2), 15.22 ppm (CH_3). *Anal*.Calcd. for $C_{26}H_{22}N_4O_4$: C, 68.71; H, 4.88; N. 12.33. Found: C, 68.68; H, 4.89; N, 12.34

Method B: From Acid Amide 6. The acid amide **6a** (0.335 g, 1 mmol) and phenylisocyanate (0.2 mL, 1.8 mmol) were refluxed in xylene for 5 h. After the solvent was evaporated, the residue was recrystallized from methanol to give 0.118 g (65 %) of **6c**, identical in mp and IR spectrum with that product obtained as described above.

3-Cyano-1,5-diphenyl-1*H*-pyrazole-4-carboxylic acid ethyl ester (7). A cold solution of acid amide **6a** (0.335 g, 1 mmol) in a mixture of DMF (0,7 mL) and $SOCl_2$ (0,15 mL) was stirred at 0-5°C for 2 h. After heating to room temperature, stirring was continued overnight, then the reaction mixture was poured over crushed ice and the separated solid isolated by filtration, washed with water and crystallized from methanol to give 0.174 g (55 %) of **7** mp 112°C; IR: 3080 cm^{-1} (Ar-H), 2927 cm^{-1} (R-H), 2263 cm^{-1} (CN), 1753 cm^{-1} (C=O); ^{1}H nmr ($CDCl_3$): δ = 7.43-7.17 (m, 10H, Ar-H), 4.29 (q, *J* = 7.1 Hz, 2H, OCH_2), 1.29 ppm (t, *J* = 7.1 Hz, 3H, CH_3); ^{13}C nmr ($CDCl_3$): δ = 162.41 (C=O), 148.64 (N-Ph), 143.88 (C-3), 140.21 (C-5), 132.44, 131.94, 131.10, 130.27, 129.45, 129.16, 127.34, 118.67 (C-4), 114.63 (CN), 63.21 (O CH_2), 15.86 ppm (CH_3). *Anal*. Calcd. for $C_{19}H_{15}N_3O_2$: C, 71.91; H, 4.76; N. 13.24. Found: C, 71.87; H, 4.76; N, 13.25.

2,3-Diphenyl-5,6-dihydro-2*H*-pyrazolo[3,4-*d*]pyridazine-4,7-dione (8). The compound **2** (0.336 g, 1 mmol) in hydrazine hydrate used as solvent was refluxed for approximately 6 h. After cooling, the formed white precipitates were collected by filtration and recrystallized from acetic acid to give 0.116 g (38 %) of **8a**, identical ir spectrum with literature compound, mp 315°C (Reference [12], mp 310°C). ^{13}C nmr (DMSO-d_6): δ = 156.01 (b, C=O), 150.55 (b, C=O), 142.81, 142.04, 139.27, 131.21, 129.80, 129.63 (2 C), 128.40, 127.57, 126.75, 113.81 ppm. *Anal*.Calcd. for $C_{17}H_{12}N_4O_2$: C, 67.10; H, 3.97; N. 18.41. Found: C, 67.05; H, 3.97; N, 18.42.

1,2-Bis-(4-ethoxycarbonyl-1,5-diphenyl-3-pyrazoloyl)-hydrazine (9). To the solution of acid chloride **3** (0.354 g 1 mmol) in CCl_4 was added anhydrous hydrazine (0.05 ml, 1 mmol) at room temperature, with stirring and the stirring continued for 30 min. at room temperature. The formed precipitate was isolated by filtration and recrystallized from ethanol to give 0.205 g (30 %) of **9**, mp 240°C; IR: 3500-2500 cm^{-1} (b, O=C-NH⇆HO-C=N-), 1684 cm^{-1} (C=O), 1630 cm^{-1} (C=O); ^{1}H nmr ($CDCl_3$): δ = 11.98 (br, 1H, NH), 7.36-7.20 (m, 10H, Ar-H), 4.18 (q, *J* = 7.1 Hz, 2H, OCH_2), 0.94 ppm (t, *J* = 7.1 Hz, 3H, CH_3); ^{13}C-nmr ($CDCl_3$): δ = 166.15 (C=O), 157.95 (C=O), 148.89 (N-Ph), 146.26 (C-3), 140.62 (C-5), 132.22, 131.29, 131.04, 130.77, 130.51, 130.13, 127.66, 115.14 (C-4), 63.52 (OCH_2), 15.55 ppm (CH_3). *Anal*.Calcd. for $C_{38}H_{32}N_6O_6$: C, 68.25; H, 4.82; N. 12.57. Found: C, 68.30; H, 4.83; N, 12.56.

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