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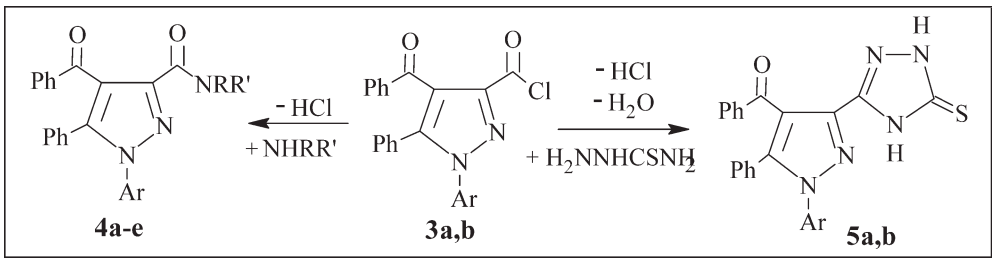
Received June 16, 2009
DOI 10.1002/jhet.306
Published online 23 February 2010 in Wiley InterScience (www.interscience.wiley.com).



The 1*H*-pyrazole-3-carboxylic acids **2** were converted via reactions of their acid chlorides **3** with some semi- and thiosemicarbazide derivatives into the corresponding new phenylsemi- and thiosemicarbazides **4a–e**, **6**, 5-(pyrazol-3-yl)-4*H*-1,2,4-triazol-3-thiones **5a**,**b**, and 2-(pyrazol-3-yl)-1,3,4-thiadiazol **7** derivatives, in good yields (45-97%, respectively). The reactions of **4a,c,e** with *Lawesson* reagent lead to the products **6** and **7** formation. The structures of these newly synthesized compounds were determined from the IR, ^{1}H- and ^{13}C-NMR spectroscopic data and elemental analyses.

J. Heterocyclic Chem., **47**, 472 (2010).

INTRODUCTION

2,3-Furandiones in general are considered as convenient and versatile synthons in heterocyclic synthesis [1,2]. A convenient method for their synthesis, the mechanism of reactions, and semiempirical (AM1 and PM3) and *ab initio* (DFT) calculations on the interaction of 4-benzoyl-5-phenyl-2,3-dihydro-2,3-furandione (**1**) with several semicarbazones, ureas, thioureas, and anilides have been reported recently [3–7]. The reactions of 2,3-furandione **1** and various hydrazines or hydrazones result in new pyrazole-3-carboxylic acids, pyrazolopyridazinones, and some of their derivatives. The pyrazole carboxylic acids can be easily transformed into the corresponding acid chloride, ester, or amide derivatives by the general chemical procedures [8–13]. Pyrazole derivatives are generally well-known nitrogen containing heterocycles, and various procedures have been developed for their syntheses [14–17].

Pyrazole derivatives are very important organic compounds because they are widely used in pharmaceuticals and agrochemicals. Their excellent control activities in regard to various plant diseases are studied [18,19]. They can also be used as antifungal [20], antibacterial [21], antimicrobial [22,23], and anti-inflammatory agents [24–28]. The possible biological properties of the pyrazol, pyridazinone, pyrazolopyridazinone [29], and oxazin derivatives make it attractive to study these compounds.

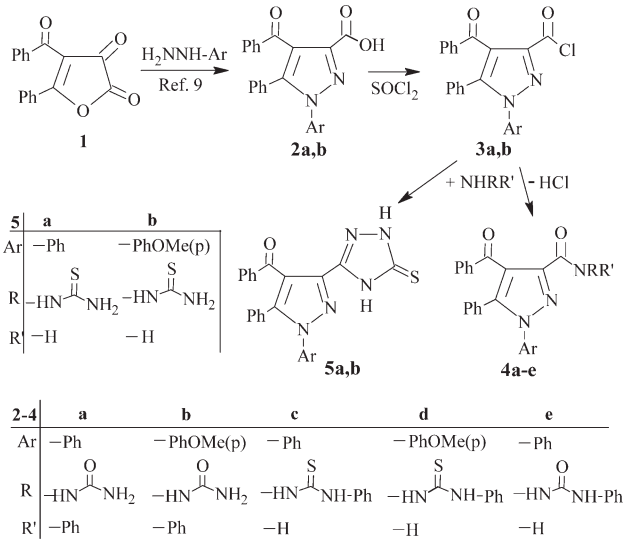
In view of these important properties, we decided both to prove reproducibility of the reaction of 4-benzoyl-1,5-diphenyl-1*H*-pyrazole-3-carboxylic acid (**2a**) and -acid chloride (**3a**) with some semi- and thiosemicarbazide derivatives and to extend our investigations related to preparing new heterocycles, which include the pyrazole ring in their structure. Here, we report the chemical behavior of **3** toward various semi- and thiosemicarbazides (see Scheme 1). As a result of these reactions, new phenylsemi- and thiosemicarbazides **4a–e**, **6**, 5-(substituted pyrazol-3-yl)-4*H*-1,2,4-triazol-3-thiones **5a**,**b**, and 2-(substituted pyrazol-3-yl)-1,3,4-thiadiazol **7** derivatives were synthesized, and their structures were identified by spectroscopic and elemental analyses.

RESULTS AND DISCUSSION

Treatment of the yellow furandione **1** with arylhydrazines under reflux in benzene for 1–6 h, the corresponding white coloured 1*H*-pyrazole-3-carboxylic acids **2** [8] were obtained. The compounds **2** can easily be transformed into the corresponding 1*H*-pyrazole-3-carboxylic acid chloride **3** by usual chemical procedures [9]. Substituted 2,3-furandione **1**, -acid **2** and -acid chloride **3**, which are used as an important initial materials in the synthesis of the target heterocycles, were prepared using the literature procedures (**2b** and **3b** were synthesized by us, yet) [1,8,9,15] (see Scheme 1).

The compounds **3** treatment with various semi- and thiosemi-carbazide derivatives in boiling benzene or xylene gave the corresponding new structures **4**,**5** as main

Scheme 1

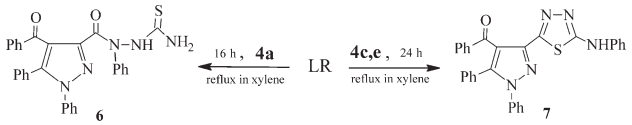


product. The progress of the reactions was monitored by thin-layer chromatography until complete consumption of the starting materials. The compounds **4a–e**, **5a**,**b** were obtained in excellent yields (70–97%), except **5a** (45%), after evaporation of the organic solvents and recrystallization from proper solvent (like methanol or butanol, see Experimental part). The reaction of the compound **3b** with 1-phenylsemicarbazide led to the formation of **4b**, under reflux in xylene for 8 h, in 76% yield without opening the pyrazole ring. To make the reaction selective, we had to determine its parameters, in other words, the reaction pathway, leading to such results. The excellent yield of the reaction can be explained by the chemical behavior of the compound **3** toward H-active nucleophiles, such as semi- and thiosemicarbazides. It should start with a nucleophilic attack of the nitrogen atoms' lone pair electrons of the semicarbazide to the antibonding (π*) orbital at the carbonyl carbon at C3 position of the pyrazol ring. Simultaneous attack of the other nitrogen atoms of the semicarbazide to the carbonyl carbon of the **3** could form some by-products. We assume that the reaction occurs under thermodynamic control. The by-products formed in this way are removed when the raw products are treated with diethyl ether. Previously, analogs reactions have been reported with hydrazines, ureas, diamines, aminophenols, and the corresponding open chain compounds [9–13]. In the IR spectrum of compound **4b**, the ═NH absorption bands were observed between 3480 and 3300 cm^{-1}, and the C═O absorption was at 1682 cm^{-1}. The ^{1}H-NMR signals were found at δ equal to 9.09 ppm (s, 1H, NH), 7.68–6.92 (m, 19H, ArH), 6.20 (b, 2H, NH_2), and 3.77 ppm (s, 3H, OCH_3), and ^{13}C NMR signals at δ such as 190.56 (t, PhCO), 159.98, 158.23 (two s, C═O), 159.50 (C─OCH_3), 144.28, 143.45 (C-3, C-5), 118.40 (C-4), and 55.90 ppm (q, OCH_3). Finally, the elemental analysis data along with spectroscopic data (details see Experimental) confirm the structure of **4b**.

Interaction of the pyrazole-3-carboxylic acid chlorides **3** with some semi- and thiosemicarbazide derivatives at reflux results in the corresponding new products **4a–e**. Surprisingly, using thiosemicarbazide in reaction with **3**, the 5-(substituted pyrazol-3-yl)-4*H*-1,2,4-triazol-3-thione derivatives **5a**,**b** were obtained exclusively. At this point, the reaction of **3** with thiosemicarbazide in boiling benzene for 4 h with no catalytic amounts of pyridine or triethylamine gave the product **5a**, which was obtained in 65% yield by recrystallizing from *n*-butanol (see Scheme 1). The moderate to good yield of the reaction can be explained by the chemical behavior of acid chlorides, similar to the behavior of the compound **3** toward *N*-nucleophiles [8–13]. The formation of **5** can easily be explained by a nucleophilic attack on the carbonyl group of the acid chloride **3**. It appears, that this process can be followed by elimination of a molecule of hydrogen chloride, and finally, loss of a molecule of water, to give **5**, whose formation is confirmed by TLC using authentic specimens of **5** and strongly supported by the results of all analytical and spectroscopic measurements. A Beilstein test did not give a green colour for compound **5**. The IR spectrum of **5a** showed characteristic absorption bands between 3500 and 2900 cm^{-1} (b, NH), and at 1662 cm^{-1} (s, CO). The ^{1}H-NMR signals were found to be at δ equal to 10.49 (b, 1H, NH), 9.34 (b, 1H, NH), 7.77–7.08 ppm (m, 15H, ArH), and the ^{13}C-NMR signals at δ such as 191.70 (t, PhC═O), 159.84 (C═S), 154.68–114.88 (arom. C's), 144.27, 143.66 (C-3, C-5), and 123.08 ppm (C-4).

To examine, if that kind of chemistry can be extended to somewhat modified systems, several attempts to change functional groups in **4** have now been made, e.g. transformation of carbonyl groups into the corresponding C═S-moieties using the *Lawesson* reagent [2,4-bis-(4-methoxyphenyl) 1,3,2,4-dithiadiphosphetane-2,4-disulfide] [30–33]. According to the usual experimental procedures applied to achieve sulfurization of carbonyls with aid of the Lawesson reagent (LR) [30–33], the phenylsemicarbazide derivatives **4a**, **4c,** or **4e** and LR were refluxed in dry xylene on an oil bath for 16 or 24 h, thus, forming a yellow solution. After cooling, white coloured crystals (**6**) or yellow needles (**7**) could be obtained in moderate yields (39–20%). Surprisingly, the outcome of these experiments did not follow the expected routes, but novel, potential, and biologically active pyrazole derivated heterocycles were obtained from those reactions as shown in Scheme 2.

Scheme 2



CONCLUSION

This article reported the facile synthesis of new phenylsemi- and thiosemicarbazides **4a–e**, **6**, 5-(substituted pyrazol-3-yl)-4*H*-1,2,4-triazol-3-thiones **5a**,**b**, and 2-(substituted pyrazole-3-yl)-1,3,4-thiadiazol **7** derivatives from the nucleophilic substitution or recyclization of a pyrazole-3-carbonyl chlorides **3** with various semi- and thiosemicarbazides. The products were easily purified and obtained with a good yield and characterized by spectroscopic techniques as well as microanalyses. All newly synthesized compounds are soluble in most of organic solvents, but their limited solubility in most of inorganic solvents could be a drawback for subsequent applications. However, it may happen these compounds possess interesting biological properties [18–29] that would deserve further investigations. These functionalized products are amenable to further transformations, and we anticipate that they may have important applications in medicinal and synthetic organic chemistry.

EXPERIMENTAL

Melting points are uncorrected and recorded on Electrothermal 9200 digital melting point apparatus. Microanalyses were performed on a Leco-932 CHNS-O Elemental Analyser. A Jasco 460 Plus FTIR and a Shimadzu FTIR-8400 model spectrophotometers were used for IR spectra (in the range of 400–4000 cm^{-1} region), using KBr pellets or ATR techniques. The ^{1}H-and ^{13}C-NMR spectra were measured with Bruker 300 MHz and Bruker Avance III 400 MHz spectrometers and the chemical shifts were recorded in ppm units. After completion of the reactions, solvents were evaporated with rotary evaporator (Buchi RE model 111). The reactions were followed by TLC using DC Alufolien Kieselgel 60 F_{254} Merck and Camag TLC lamp (254/366 nm). Solvents and all other chemical reagents were purchased from Merck, Sigma, Aldrich and Fluka and used directly without further purification. Solvents were dried by refluxing with the appropriate drying agents and distilled before use.

4-Benzoyl-5-phenyl-1-*p*-methoxyphenyl-1*H*-pyrazole-3-carboxylic acid (2b). A mixture of furandione **1** (0.28 g, 1 mmol) and 4-methoxyphenylhydrazine hydrochloride (0.17 g, 1 mmol) was refluxed in 30 mL of dry benzene for 6 h by adding 2–3 drops pyridine. After cooling, the precipitate was filtered off and treated with dry ether to give a crude solid that was recrystallized from methanol. The yield 0.25 g (63%) of **2b**, mp 232°C; IR (ATR): 3400–2400 (b, OH, COOH), 3065, 3030 (arom. CH), 2951–2897 (aliph. CH), 1674 (s br, CO's), 1604–1464 (phenyl and pyrazole rings C⋯C, C⋯N), 1248 cm^{-1} (C—O); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.69–6.81 (m, 14H, ArH), 3.86 ppm (s, 3H, OCH_3); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 183.34 (t, PhC=O), 170.15 (s, COOH), 159.75 (MeO—Ph), 158.75 (N—Ph), 143.90, 143.12 (C-3, C-5), 139.82 (C—Ph), 134.99, 134.25, 132.03, 130.51, 128.90, 128.63, 128.44, 128.13, 128.10, 127.60, 127.28, 127.25 (C—Ph), 116.50 (s, C-4), 114.02, 114.00 (C—Ph), 55.53 ppm (q, OCH_3). Anal. Calcd. for $C_{24}H_{18}N_2O_4$ (398.41): C, 72.35; H, 4.55; N, 7.03. Found: C, 72.13; H, 4.72; N, 6.94.

4-Benzoyl-5-phenyl-1-*p*-methoxyphenyl-1*H*-pyrazole-3-carbonyl chloride (3b). Compound **2b** (0.40 g, 1 mmol) and thionyl chloride (1 mL, 13.8 mmol) were refluxed on a steam bath for 6 h. After cooling, the crude precipitate formed was filtered off and recrystallized from xylene or toluene, yield 0.31 g (68%), mp 177°C; IR (ATR): 3060, 3013 (arom. CH), 2967–2870 (aliph. CH), 1761, 1648 (s, CO), 1595–1454 (phenyl and pyrazole rings C⋯C, C⋯N), 1250 cm^{-1} (C—O); ^{1}H-NMR (400 MHz, DMSO-d_6): δ 7.80–6.74 (m, 14H, ArH), 3.78 ppm (s, 3H, OCH_3). ^{13}C-NMR (100 MHz, DMSO-d_6): δ 191.35 (t, J = 4.4 Hz, PhCO), 162.75 (s, COCl), 159.61 (MeO—Ph), 143.44, 142.58 (C-3, C-5), 138.15 (C—Ph), 133.81, 132.05, 130.08, 129.59, 129.49, 129.06, 128.83, 128.30, 127.75, 127.60 (C—Ph), 122.97 (s, C-4), 114.60 (C—Ph), 55.90 ppm (q, OCH_3). Anal. Calcd. for $C_{24}H_{17}N_2O_3Cl$ (416.86): C, 69.15; H, 4.11; N, 6.72. Found: C, 69.23; H, 4.29; N, 6.60.

1-[(4-Benzoyl-1,5-diphenyl-1*H*-pyrazol-3-yl)carbonyl]-1-phenylsemicarbazide (4a). Acid chloride **3a** (0.39 g, 1 mmol) and 1-phenylsemicarbazide (0.15 g, 1 mmol) were refluxed in xylene on an oil bath for 2 h. After cooling, the crude precipitate that formed was filtered off and recrystallized from methanol, yield 0.44 g (88%) of **4a**, mp 232–233°C; IR (KBr): 3488, 3334, 3256 (NH⇄OH and NH_2), 3057 (aromatic CH), 1713, 1658 (s, CO), 1597–1452 cm^{-1} (C⋯C, C⋯N); ^{1}H-NMR (300 MHz, DMSO-d_6): δ 9.10 (s, 1H, NH), 7.58–7.10 (m, 20H, ArH), 6.19 ppm (b, 2H, NH_2); ^{13}C-NMR (75 MHz, DMSO-d_6): δ 190.50 (t, J = 4.3 Hz, PhCO), 159.13 (s, C=O), 158.21 (C=O), 155.83 (N—Ph), 143.42, 142.54 (C-3, C-5), 138.95 (C—Ph), 134.52, 133.18, 132.11, 131.86, 130.53, 129.59, 129.03, 128.82, 128.67, 128.56, 128.26, 126.08 (C—Ph), 122.51, 119.94 ppm (C-4). Anal. Calcd. for $C_{30}H_{23}N_5O_3$ (501.54): C, 71.84; H, 4.62; N, 13.96. Found: C, 72.03; H, 4.79; N, 13.64.

1-[(4-Benzoyl-5-phenyl-1-*p*-methoxyphenyl-1*H*-pyrazol-3-yl) carbonyl]-1-phenylsemicarbazide (4b). Acid chloride **3b** (0.42 g, 1 mmol) and 1-phenylsemicarbazide (0.15 g, 1 mmol) were refluxed in xylene on an oil bath for 8 h. After evaporation, the oily residue obtained was treated with dry ether. The crude product formed was filtered off and recrystallized from a mixture of benzene-cyclohexane (1:3), yield 0.40 g (76%) of **4b**, mp 129°C; IR (ATR): 3480, 3383, 3309 (NH⇄OH and NH_2), 3065, 2912, 2849 (arom. and aliph. CH), 1682 (s br, CO's), 1590–1447 (C⋯C, C⋯N), 1248 cm^{-1} (C—O); ^{1}H-NMR (400 MHz, DMSO-d_6): δ 9.09 (s, 1H, NH), 7.68–6.92 (m, 19H, ArH), 6.20 (b, 2H, NH_2), 3.77 ppm (s, 3H, OCH_3); ^{13}C-NMR (100 MHz, DMSO-d_6): δ 190.56 (t, J = 4.2 Hz, PhCO), 159.98 (s, C=O), 159.50 (MeO—Ph), 158.23 (C=O), 155.30 (N—Ph), 144.28, 143.45 (C-3, C-5), 141.15 (C—Ph), 138.17, 134.21, 132.10, 131.93, 130.55, 130.08, 129.49, 128.92, 128.76, 128.15, 127.96, 127.59, 126.79 (C—Ph), 124.91, 118.40 (C-4), 116.61 (C—Ph), 55.90 ppm (q, OCH_3). Anal. Calcd. for $C_{31}H_{25}N_4O_4$ (517.55): C, 71.94; H, 4.87; N, 10.83. Found: C, 72.03; H, 4.77; N, 10.68.

1-[(4-Benzoyl-1,5-diphenyl-1*H*-pyrazol-3-yl)carbonyl]-4-phenylthiosemicarbazide (4c). Acid chloride **3a** (0.30 g, 0.8 mmol) and 4-phenylthiosemicarbazide (0.13 g, 0.8 mmol) were refluxed in benzene for 1 h. After cooling, the crude precipitate that formed was filtered off and recrystallized from *n*-butanol to give 0.27 g of **4c** (68%), mp 250–251°C; IR (KBr): 3393, 3209 (NH⇄OH ve NH), 3065 (arom. CH), 2415 (w, tautomeric SH), 1674 (CO), 1610–1460 (C⋯C, C⋯N), 1360 cm^{-1} (C=S); ^{1}H-NMR (400 MHz, DMSO-d_6): δ 12.61 (s, 1H, NH⇄SH), 10.02 (b, 1H, NH), 9.72 (b, 1H, NH), 7.54–6.92 ppm (m, 20H, ArH); ^{13}C-NMR (100 MHz, DMSO-d_6): δ 191.50 (t, J = 4.4 Hz, PhCO), 161.63 (C=S), 158.26 (C=O, amide), 156.60 (N—Ph), 145.17, 142.56 (C-3, C-5 exchangeable), 140.24 (C—Ph), 138.86, 137.06, 133.96, 130.46, 129.11, 128.99, 128.91, 128.60, 128.18, 127.87, 127.71, 126.13 (C—Ph), 123.17 (C-4), 117.08, 116.88 ppm (C—Ph). Anal. Calcd. for $C_{30}H_{23}N_5O_2S$ (517.60): C, 69.61; H, 4.48; N, 13.53; S, 6.19. Found: C, 69.88; H, 4.80; N, 13.91; S, 6.00.

1-[(4-Benzoyl-5-phenyl-1-*p*-methoxyphenyl-1*H*-pyrazol-3-yl) carbonyl]-4-phenylthiosemicarbazide (4d). Acid chloride **3b** (0.42 g, 1 mmol) and 4-phenylthiosemicarbazide (0.17 g, 1 mmol) were refluxed in xylene for 6 h. After evaporation, the oily residue obtained was treated with dry ether. The crude product formed was filtered off and recrystallized from *n*-butanol to give 0.38 g of **4d** (70%), mp 202°C; IR (ATR): 3400–3100 (NH⇄OH and NH), 3065, 2966, 2873 (C—H), 2450 (w, tautomeric SH), 1674 (s br, CO's), 1604–1475 (C⋯C, C⋯N), 1370 cm^{-1} (C=S); ^{1}H-NMR (400 MHz, DMSO-d_6): δ 12.59 (s, 1H, NH⇄SH), 10.39 (b, 1H, NH), 9.96 (t, 1H, NH), 7.74–6.92 (m, 19H, ArH), 3.76 ppm (s, 3H, OCH_3); ^{13}C-NMR (100 MHz, DMSO-d_6): δ 191.30 (t, J = 4.2 Hz, PhCO), 160.06 (C=S), 159.85 (MeO—Ph), 159.61 (C=O, amide), 156.62 (N—Ph), 144.07, 142.19 (C-3, C-5 exchangeable), 140.68 (C—Ph), 138.15, 137.63, 134.74, 133.63, 132.19, 131.03, 130.17, 129.58, 129.22, 128.85, 128.56, 128.33, 128.13, 127.85, 127.77, 126.39 (C—Ph), 122.09 (C-4), 117.86, 116.88, 114.52 (C—Ph), 55.90 ppm (q, OCH_3). Anal. Calcd. for $C_{31}H_{25}N_4O_3S$ (533.62): C, 69.77; H, 4.72; N, 10.50; S, 6.01. Found: C, 69.85; H, 4.80; N, 10.32; S, 6.14.

1-[(4-Benzoyl-1,5-diphenyl-1*H*-pyrazol-3-yl)carbonyl]-4-phenylsemicarbazide (4e). Acid chloride **3a** (0.30 g, 0.8 mmol) and 4-phenylsemicarbazide (0.15 g, ∼0.8 mmol) were refluxed in benzene for 4 h. After cooling, the crude precipitate was filtered off and recrystallized from *n*-butanol, yield 0.40 g (97%) of **4e**, mp 219°C; IR (KBr): 3435, 3329 (NH⇄OH), 3060 (arom. CH), 1696, 1641 (s, CO), 1601–1478 cm^{-1} (C⋯C, C⋯N); ^{1}H-NMR (300 MHz, $CDCl_3$/DMSO-d_6): δ 9.79 (s, 1H, NH), 8.37 (s, 1H, NH), 7.99 (s, 1H, NH), 7.71–6.85 ppm (m, 20H, ArH); ^{13}C-NMR (75 MHz, $CDCl_3$/DMSO-d_6): δ 190.26 (t, J = 4.3 Hz, PhCO), 159.51, 154.52 (HNC=O), 143.16, 142.70 (C-3, C-5), 138.48, 137.87, 137.09, 132.21, 128.87, 128.46, 128.21, 127.88, 127.76, 127.68, 127.47, 126.96, 124.65 (C—Ph), 121.37, 121.18, 117.62 ppm (C-4). Anal. Calcd. for $C_{30}H_{23}N_5O_3$ (501.54): C, 71.84; H, 4.62; N, 13.96. Found: C, 71.47; H, 4.77; N, 14.21.

5-(4-Benzoyl-1,5-diphenyl-1*H*-pyrazol-3-yl)-4*H*-1,2,4-triazol-3-thione (5a). Acid chloride **3a** (0.50 g, 1.3 mmol) and thiosemicarbazide (0.12 g, 1.3 mmol) were refluxed in benzene for 4 h. After cooling, the crude precipitate was filtered off and recrystallized from *n*-butanol, yield 0.36 g (65%) of **5a**, mp 208°C; IR (KBr): 3600–2900 cm^{-1} (b, NH, peak max.: 3468, 3339, 3182), 3055 (arom. CH), 1662 (s, CO), 1602–1497 (C⋯N, C⋯C), 1367 cm^{-1} (C=S); ^{1}H-NMR (400 MHz, DMSO-d_6): δ 10.49 (b, 1H, NH), 9.34 (b, 1H, NH), 7.77–7.08 ppm (m, 15H, ArH); ^{13}C-NMR (100 MHz, DMSO-d_6): δ 191.70 (t, J = 4.5 Hz, PhCO), 159.84 (C=S), 154.68 (N—Ph), 144.27, 143.66, 143.25 (C-3, C-5 or C-5′ exchangeable), 140.23 (C—Ph), 139.21, 138.18, 136.39, 135.24, 133.67, 132.26, 131.75, 130.41, 129.68, 129.31, 128.91, 128.27, 127.74, 125.32 (C—Ph), 123.08 (C-4), 117.18, 114.88 ppm (C—Ph). Anal. Calcd. for $C_{24}H_{17}N_5OS$ (423.49): C, 68.07; H: 4.05; N: 16.54; S: 7.57. Found: C, 67.90; H, 4.25; N, 16.40; S. 7.30.

5-(4-Benzoyl-5-phenyl-1-*p*-methoxyphenyl-1*H*-pyrazol-3-yl)-4*H*-1,2,4-triazol-3-thione (5b). Acid chloride **3b** (0.50 g, 1.2 mmol) and thiosemicarbazide (0.11 g, 1.2 mmol) were refluxed in xylene for 8 h. After cooling, the crude precipitate was filtered off and recrystallized from a mixture of carbon tetrachloride and cyclohexane (1:3), yield 0.45 g (83%) of **5b**, mp 140°C; IR (ATR): 3320, 3156 (NH), 3057, 2935 (C—H), 2450 (w, tautomeric SH), 1670 (s, CO), 1598–1452 (C⋯C, C⋯N), 1362 cm^{-1} (C=S); ^{1}H-NMR (400 MHz, DMSO-d_6): δ 12.58 (s, 1H, NH⇄SH), 10.36 (b, 1H, NH), 7.76–6.92 (m, 14H, ArH), 3.76 ppm (s, 3H, OCH_3); ^{13}C-NMR (100 MHz, DMSO-d_6): δ 191.30 (t, J = 4.6 Hz, PhCO), 161.93 (C=S), 159.81 (MeO—Ph), 156.63 (N—Ph), 144.07, 143.47, 142.21 (C-3, C-5 or C-5′ exchangeable), 140.68 (C—Ph), 138.15, 137.87, 134.73, 133.82, 132.19, 131.87, 130.32, 129.74, 129.28, 128.86, 128.33, 127.85, 126.39 (C—Ph), 122.10 (C-4), 116.80, 114.60, (C—Ph), 55.93 ppm (q, OCH_3). Anal. Calcd. for $C_{25}H_{19}N_5O_2S$ (453.52): C, 66.21; H: 4.22; N: 15.44; S: 7.07. Found: C, 66.08; H, 4.25; N, 15.15; S. 7.33.

1-[(4-Benzoyl-1,5-diphenyl-1*H*-pyrazol-3-yl)carbonyl]-1-phenylthiosemicarbazide (6). 4a (0.50 g, 1.1 mmol) and LR (0.54 g, 1.3 mmol) were refluxed in xylene on an oil bath for 16 h. Than the solvent was evaporated and remaining oily residue was treated with dry diethyl ether to give a crude product that was recrystallized from xylene. Yield 0.20 g (39%) of **6**, mp 263°C; IR (KBr): 3600–2950, (b, NH, peak max.: 3446, 3220, 3196), 3055 (arom. CH), 1690, 1637 (CO), 1594–1472 (C⋯C, C⋯N), 1364 cm^{-1} (C=S); ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.80 (d, 1H, NH), 7.77 (d, 1H, NH), 7.66–6.86 (m, 20H, ArH and 1H, NH). Anal. Calcd. for $C_{30}H_{23}N_5O_2S$ (517.60): C, 69.61, H, 4.48, N, 13.53, S, 6.19. Found: C, 69.47, H: 4.63; N: 13.76, S: 6.04.

5-Anilino-2-(4-benzoyl-1,5-diphenyl-1*H*-pyrazol-3-yl)-1,3,4-thiadiazol (7). 4e (0.50 g, 1 mmol) and LR (0.54 g, 1.3 mmol) were refluxed in xylene on an oil bath for 24 h. Than the solvent was evaporated and remaining oily residue was treated with dry diethyl ether to give a crude product that was recrystallized from xylene. Yield 0.11 g (20%) of **7**, mp 323°C; IR (KBr): 3196 (NH), 3058 (arom. CH), 1640 (CO), 1594–1491 cm^{-1} (C⋯C, C⋯N); ^{1}H-NMR (300 MHz, DMSO-d_6): δ 14.27 (s, 1H, NH), 7.46–6.97 ppm (m, 20H, ArH);^{13}C-NMR (75 MHz, DMSO-d_6): δ 175.44 (t, J = 4.2 Hz, PhCO), 149.00 (N=C—S), 148.60 (S—C—NH), 141.60, 139.21, 137.65, 133.98, 131.07, 130.10, 129.93, 129.51, 129.25, 129.17, 128.84, 128.74, 128.58, 128.26, 128.08, 127.92, 126.96, 126.42, 126.06, 111.49 ppm (arom. C's). Anal. Calcd. for $C_{30}H_{21}N_5OS$ (499.59): C, 72.12; H, 4.24; N, 14.02; S, 6.42. Found: C, 72.40; H, 4.50; N, 13.80; S, 6.71.

Acknowledgments. The authors wish to dedicate this article to Yunus Akçamur, who passed away at 2007. This study was financially supported by Research Foundation of Erciyes University.

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