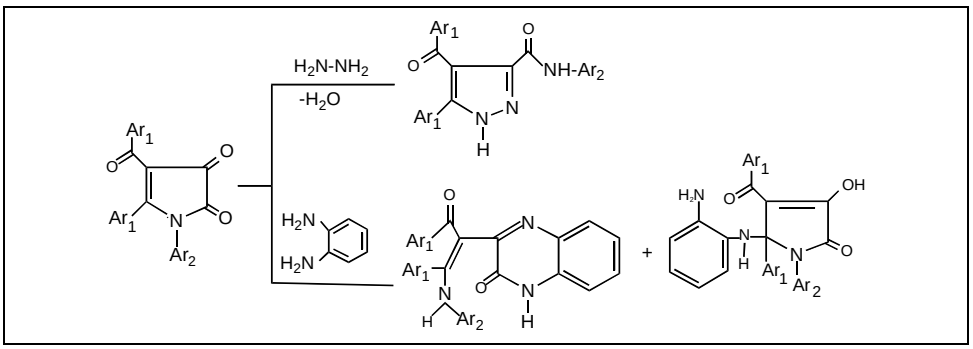
Reactions of Some Pyrrole-2,3-diones with Hydrazine Hydrate and *o*-Phenylenediamine*

Emin Sarıpınar**, Süleyman Karataş and İlhan Özer İlhan

Department of Chemistry, Arts and Sciences Faculty, Erciyes University, 38039 Kayseri-Turkey, e-mail: emin@erciyes.edu.tr, fax: 00 90 352 4378802

**Dedicated to the memory of Prof. Dr. Yunus Akçamur*

Received October 19, 2006



2,3-Dihydro-1*H*-pyrrole-2,3-diones **1a-d** react with hydrazine hydrate **2** and *o*-phenylenediamine **4** under different conditions to yield the pyrazole-3-carboxamide derivatives **3a-d**, the pyrrol-2-ones **5a-d** and the quinoxaline-2-one derivatives **6a-d**, respectively. Hydrolysis of the quinoxaline-2-one derivatives **6a-d** gave a substituted furo[2,3-*b*]quinoxaline **7**. The structures of the synthesized compounds were assigned on the basis of analytical results as well as spectroscopic data.

J. Heterocyclic Chem., **44**, 1065 (2007).

INTRODUCTION

4-Acyl substituted heterocyclic 2,3-diones, *e.g*. 2,3-dihydro-1*H*-furan-2,3-diones or 2,3-dihydro-1*H*-pyrrole-2,3-diones adds various isocyanides [1], isocyanates [2], carbodiimides [3], ketenimines [4], diphenylketene [5], imines [6], and alkenes [7], *via* [2+2], [4+1], or [4+2] cycloaddition processes affording novel mono- and bicyclic systems. *N*-Phenylimino-2,3-dihydro-1*H*-furan-2,3-diones, obtainable *e.g*. by the reactions of 4-acyl-2,3-dihydro-1*H*-furan-2,3-diones with tosyl-sulfinylamines or arylalkylcarbo-diimides or -imines, thermally rearrange to 4-acyl-2,3-dihydro-1*H*-pyrole-2,3-diones [3a,6b]. The thermal decarbonylation of 4-acyl-2,3-dihydro-1*H*-pyrrole-2,3-diones leads to the formation of highly reactive acyl(*N*-arylimidoyl)-ketenes [8]. In general, the pyrazole nucleus and its chemistry [9] have found considerable attention during the decades due to outstanding biological activities such as antipyretic, analgetic, anti-fungal and anti-inflammatory activities [10], as well as to interesting properties in commercially important dyestuffs [11]. Quinoxaline derivatives are an important class of nitrogen-containing heterocycles and they constitute useful intermediates in organic synthesis. Some of them are applied for dyes [12] and for building blocks in the synthesis of organic semiconductors [13] and show interesting biological properties (antibacterial, antiviral, anticancer, antifungal, antihelmintic, insecticidal) [14]. Oxidation of both nitrogens of the quinoxaline ring dramatically increased the diversity of certain biological properties, such as antibacterial activity [15] and hypoxia-selective anticancer activity [16]. Recently, reactions of cyclic oxalyl compounds have been reported to give corresponding heterocyclic compounds [17].

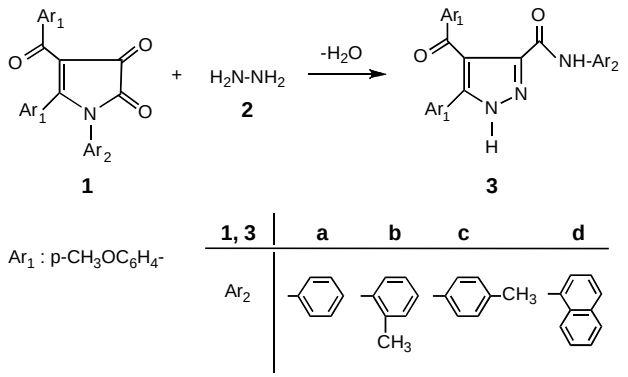
RESULTS AND DISCUSSION

In the present study, we carried out the reaction of the 2,3-dihydro-1*H*-pyrrol-2,3-diones **1a-d**, easily made from 2,3-dihydro-1*H*-furan-2,3-dione with Schiff bases at 60-70 °C furnish [18], with hydrazine hydrate (**2**) and *o*-phenylenediamine (**4**) yielding pyrazole-3-carboxamide derivatives **3a-d**, the pyrrol-2-ones **5a-d** and the quinoxaline-2-one derivatives **6a-d**, respectively. Hydrolysis of the quinoxaline-2-ones derivatives **6a-d** gave corrresponding furo[2,3-*b*]quinoxaline **7**. The reaction equations are shown in schemes. The structures of synthesized compounds were assigned on the basis of analytical results as well as spectroscopic data.

The reaction of the 2,3-dihydro-1*H*-pyrrol-2,3-diones **1a-d** with hydrazine hydrate **2** (Scheme I) yields pyrazole-3-carboxamide derivatives **3a-d**. Product **3a** obtained in 45% yield by treating **1a** with hydrazine hydrate **2** and refluxing in benzene for 1 h. The moderate yield of the reaction can be explained by the chemical behaviour of pyrrolediones **1a-d** towards H-active nucleophiles. In compounds **1a-d** carbon atoms C-2, C-3 and C-5

represent electrophilic sites of different reactivity and could be used for the construction of new heterocyclic systems upon reaction with nucleophiles, as furandiones [19]. It should start with a nucleophilic attack of the lone pair electrons of nitrogen atom of **2** at the antibonding orbital of π* of C5 position of the pyrrolediones ring similar to a Michael-type addition. In the ir spectrum of compound **3a** the -NH absorption band was found to be at *ca*. 3450-3250 cm^{-1}. The C=O absorption was at 1700 cm^{-1}. The ^1H nmr signals were at δ 12.81 and 10.50 (-NH) and 7.75-6.66 ppm (m, ArH) and the ^{13}C nmr signals were found to be at δ 194.99 (PhCO), 165.88 (N-C=O), 159.67 (C-3), 161.96 ppm (C-5) and elemental analysis data confirm the structure of **3a**.

Scheme I

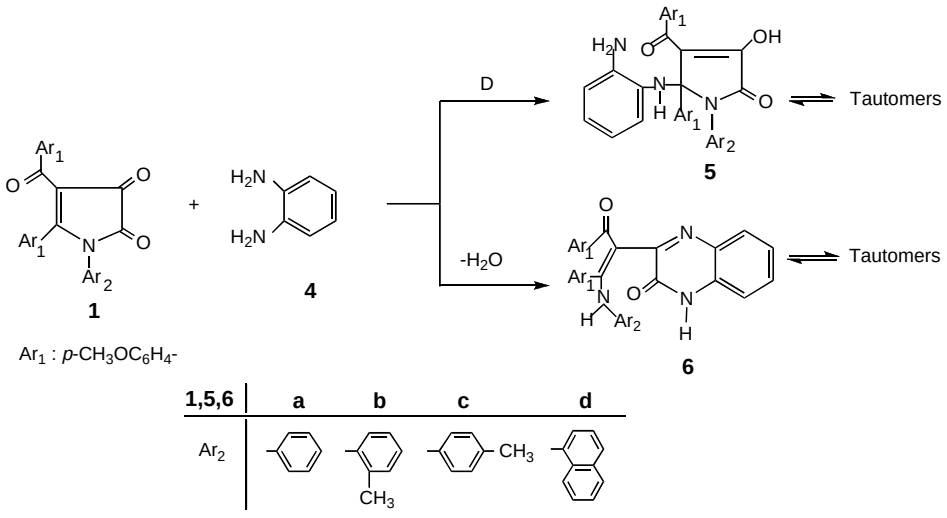


The reaction of **1a-d** with **4** are depending on the reaction temperatures, **5a-d** are obtained from refluxed solution, **6a-d** are obtained at room temperature. In the ir spectrum of compound **5a**, -OH and -NH absorption bands were found to be at 3610-3380 cm^{-1}, the C=O absorption bands were seen at 1719 and 1675 cm^{-1}, respectively. The ^1H nmr signals were found to be at δ 12.58 and 9.78 (s, 2H, -NH), 9.39 (s, enol-OH), 8.12-6.74 (m, ArH), 6.24 (s, keto-CH), 3.86 and 3.76 ppm (q, 6H, -OCH_3). The ^{13}C nmr signals were at δ 191.24 (Ar-C=O), 181.01 (C-3), 164.46 (C-2), 149.32-121.92 (aromatic C), 116.15 (C-4), 99.53 (C-5) and 57.35 ppm ($2CH_3O$).

The nucleophilic addition of *o*-phenylenediamine **4** to pyrrol-2,3-diones **1a-d** provided quinoxaline-2-ones **6a-d** in 65-73% yields. All reactions were carried out at room temperature in inert solvent [20]. These products arise from the sequential attacks of the aromatic diamine to the C-3 and C-2 atoms of the pyrrole-2,3-diones **1a-d** respectively, followed by elimination of water and ring opening of the pyrrole-2,3-dione. Therefore, the presence of tautomeric forms of **6a-d**, as well as the stability of the compounds of **6a-d** were also confirmed by these reactions, outlined briefly in Scheme II. The ^{13}C nmr spectrum of **6a** exhibits significant line broadenings for the aryl carbonyl (195.98 ppm), lactam C (158.01 ppm), C-3 (155.51 ppm), respectively. In the ir spectrum of **6a**, characteristic absorption bands at about 3400-3250 cm^{-1} NH, 1670 and 1610 cm^{-1} (C=O) were observed, as well as, the ^1H nmr spectrum of **6a** shows that (NH) protons appear at 12.40 and 11.9 ppm, respectively. Other spectral and analytical data of **6a-d** are in full agreement with their proposed structures as well.

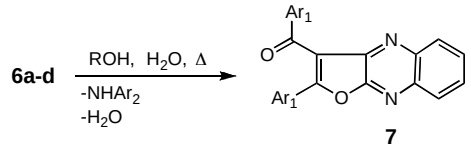
Also the hydrolysis of **6a-d** in *n*-butyl alcohol leads to corresponding furo[2,3-*b*]quinoxaline **7**, the C=O absorption band were found to be at about 1650 cm^{-1}.

Scheme II



The ^1H nmr signals were found to be at δ 8.16-6.90 (m, 12H, ArH), 3.87 and 3.65 ppm (s, 6H, $2CH_3O$) (Scheme III).

Scheme III



Ar_1 : *p*-$CH_3OC_6H_4$-

EXPERIMENTAL

Solvents were dried by refluxing over the appropriate drying agent and distilled before use. Melting points were determined on an Electrothermal 9200 apparatus and are uncorrected. Microanalyses were performed on a Carlo Erba elemental analyser, model 1108. The ir spectra were recorded on a Shimadzu Model 435 V-04 spectrophotometer, using potassium bromide pellets. The ^1H and ^{13}C nmr spectra were recorded on Varian Gemini 200 istrument. The chemical shifts are reported in ppm from tetramethylsilane as an internal standard and are given in δ (ppm). All experiments were followed by TLC using DC Alufolien Kieselgel 60 F_{254} Merck and Camag TLC lamp (254/366 nm).

4-(4-Methoxylbenzoyl)-5-(4-methoxyphenyl)-1*H*-pyrazole-3-carboxylic phenylamide (3a). 4-(4-Methoxybenzoyl)-5-(4-methoxyphenyl)-1-phenyl-2,3-1*H*-pyrrole-2,3-dione **1a** (1.0 g, 2.42 mmol) and hydrazine hydrate **2** (0.12 g, 2.42 mmol) were refluxed in benzene (50 mL) for 1 h. or stirred in benzene at room temperature for 24 h. The solvent was evaporated and the remaining oily residue was treated with dry diethyl ether and stirred for 24 h. to give the white crude product which was recrystallized from *n*-butyl alcohol and allowed to dry on P_2O_5; resulting in yield 45% (0.46 g); mp 224-225°C; ir: 3450-3250 (b, N-H), 1700 cm^{-1} (C=O); ^1H nmr ($CDCl_3$): δ 12.81 and 10.50 (2H, -NH), 7.75-6.66 (m, 13H, ArH), 3.76 (s, 3H, CH_3) and 3.66 ppm (s, 3H, CH_3); ^{13}C nmr ($CDCl_3$): δ 194.99 (ArCO), 165.88 (N-C=O), 161.96 (C-5), 159.67 (C-3), 139.73-115.01 (aromatic C), 57.39 ppm ($2CH_3$). *Anal.* Calcd. for $C_{25}H_{21}N_3O_4$; C, 70.25; H, 4.95; N, 9.83. Found; C, 70.10; H, 5.05; N, 9.82.

4-(4-Methoxylbenzoyl)-5-(4-methoxylphenyl)-1*H*-pyrazole-3-carboxylic 2-methylphenylamide (3b). 4-(4-Methoxybenzoyl)-5-(4-methoxyphenyl)-1-(2-methylphenyl)-1*H*-pyrrole-2,3-dione **1b** (1.0 g, 2.34 mmol) and hydrazine hydrate **2** (0.12 g, 2.34 mmol) were refluxed in benzene (50 mL) for 1 h. or stirred in benzene at room temperature for 24 h. The solvent was evaporated and the remaining oily residue was treated with dry diethyl ether and stirred for 24 h. to give the white crude product which was recrystallized from *n*-butyl alcohol and allowed to dry on P_2O_5; resulting in yield 50% (0.52 g); mp 215-216°C; ir: 3500-3150 (b, N-H), 1720 cm^{-1} (C=O); ^1H nmr ($CDCl_3$): δ 12.40 and 10.11 (2H, -NH), 8.06-6.69 (m, 12H, ArH), 3.77 (s, 3H, CH_3), 3.72 (s, 3H, CH_3) and 2.45 ppm (s, CH_3); ^{13}C nmr ($CDCl_3$): δ 194.58 (ArCO), 165.86 (N-C=O), 161.89 (C-5), 159.34 (C-3), 134.56-114.89 (aromatic C), 57.40 ($2CH_3$), 20.13 ppm (CH_3). *Anal.* Calcd. for $C_{26}H_{23}N_3O_4$; C, 70.73; H, 5.25; N, 9.52. Found; C, 70.68; H, 5.37; N, 9.43.

4-(4-Methoxylbenzoyl)-5-(4-methoxylphenyl)-1*H*-pyrazole-3-carboxylic 4-methylphenylamide (3c). 4-(4-Methoxybenzoyl)-5-(4-methoxyphenyl)-1-(4-methylphenyl)-1*H*-pyrrole-2,3-dione **1c** (1.0 g, 2.34 mmol) and hydrazine hydrate (**2**) (0.12 g, 2.34 mmol) were refluxed in benzene (50 mL) for 1 h. or stirred in benzene at room temperature for 24 h. The solvent was evaporated and the remaining oily residue was treated with dry diethyl ether and stirred for 24 h. to give the white crude product which was recrystallized from *n*-butyl alcohol and allowed to dry on P_2O_5; resulting in yield 55% (0.57 g); mp 230-231°C; ir: 3450-3250 (b, N-H), 1710 cm^{-1}(C=O); ^1H nmr ($CDCl_3$): δ 12.35 and 10.47 (2H, -NH), 7.72-6.68 (m, 12H, ArH), 3.76 (s, 3H, CH_3), 3.69 (s, 3H, CH_3) and 2.31 ppm (s, CH_3); ^{13}C nmr ($CDCl_3$): δ 194.96 (ArCO), 165.81 (N-C=O), 161.90 (C-5), 159.06 (C-3), 137.44-114.89 (aromatic C), 57.39 ($2CH_3$), 22.88 ppm (CH_3). *Anal.* Calcd. for $C_{26}H_{23}N_3O_4$; C, 70.73; H, 5.25; N, 9.52. Found; C, 70.99; H, 5.45; N, 9.75.

4-(*4*-Methoxylbenzoyl)-5-(*4*-methoxylphenyl)-1*H*-pyrazole-3-carboxylic 1-naphthylamide (3d). 4-(4-Methoxybenzoyl)-5-(4-methoxyphenyl)-1-(1-naphtyl)-2,3-1*H*-pyrrole-2,3-dione **1d** (1.0 g, 2.16 mmol) and hydrazine hydrate **2** (0.11 g, 2.16 mmol) were refluxed in benzene (50 mL) for 1 h. or stirred in benzene at room temperature for 24 h. The solvent was evaporated and the remaining oily residue was treated with dry diethyl ether and stirred for 24 h. to give the white crude product which was recrystallized from *n*-butyl alcohol and allowed to dry on P_2O_5; resulting in yield 45% (0.46 g); mp 136.5-138°C; ir: 3500-3250 (b, N-H), 1725 cm^{-1}(C=O); ^1H nmr ($CDCl_3$): δ 12.38 and 10.73 (2H, -NH), 8.29-6.65 (m, 15H, ArH), 3.75 (s, 3H, CH_3), and 3.68 ppm (s, 3H, CH_3); ^{13}C nmr ($CDCl_3$): δ 194.85 (ArCO), 165.89 (N-C=O), 161.89 (C-5), 160.12 (C-3), 136.11-114.72 (aromatic C), and 57.19 ppm ($2CH_3$). *Anal.* Calcd. for $C_{29}H_{23}N_3O_4$; C, 72.94; H, 4.85; N, 8.80. Found; C, 72.97; H, 4.89; N, 8.58.

5-(2-Aminophenyl)amino-3-hydroxy-4-(4-methoxylbenzoyl)-5-(4-methoxylphenyl)-1-phenyl-2,5-dihydro-2*H*-pyrrol-2-one (5a). 4-(4-Methoxybenzoyl)-5-(4-methoxyphenyl)-1-phenyl-2,3-1*H*-pyrrole-2,3-dione **1a** (1.0 g, 2.42 mmol) and *o*-phenylenediamine **4** (0.26 g, 2.42 mmol) were refluxed in benzene (50 mL) for 1 h. The solvent was evaporated and the remaining oily residue was treated with dry diethyl ether and stirred for 24 h. to give the yellow crude product which was recrystallized from *n*-butyl alcohol and allowed to dry on P_2O_5; resulting in yield 55% (0.69 g); mp 184°C; ir: 3610-3380 (br, NH and OH), 3360 (NH_2), 1719, 1675 (C=O); ^1H nmr (DMSO-d_6): δ 12.58 (br, -NH) , 9.78 (s, -NHO), 9.39 (s, enol-OH), 8.12-6.74 (m, 17H, Ar-H), 6.24 (s, keto-CH), 3.86 (s, 3H, CH_3), and 3.76 ppm (s, 3H, CH_3O); ^{13}C nmr (DMSO-d_6): δ 191.24 (ArCO), 181.01 (C-3), 164.46 (C-2), 149.32-121.92 (aromatic C), 116.15 (C-4), 99.53 (C-5), and 57.35 ppm ($2CH_3O$). *Anal.* Calcd. for $C_{31}H_{27}N_3O_5$; C, 71.39; H, 5.22; N, 8.06. Found; C, 71.45; H, 5.48; N, 7.85.

5-(2-Aminophenyl)amino-3-hydroxy-4-(4-methoxylbenzoyl)-1-(2-methylphenyl)-5-(4-methoxyphenyl)-2,5-dihydro-2*H*-pyrrol-2-one (5b). 4-(4-Methoxybenzoyl)-5-(4-methoxyphenyl)-1-(2-methylphenyl)-1*H*-pyrrole-2,3-dione **1b** (1.0 g, 2.34 mmol) and *o*-phenylenediamine **4** (0.25 g, 2.34 mmol) were refluxed in benzene (50 mL) for 1 h. The solvent was evaporated and the remaining oily residue was treated with dry diethyl ether and stirred for 24 h. to give the yellow crude product which was recrystallized from *n*-butyl alcohol and allowed to dry on P_2O_5; resulting in yield 55% (0.69 g); mp 204°C; ir: 3620-3380 (br, NH and OH), 3370 (NH_2), 1711, 1680 (C=O); ^1H nmr (DMSO-d_6): δ 12.61 (br, -NH) , 9.77 (s, -NHO), 9.32 (s, enol-OH), 8.10-6.75 (m, 16H, Ar-H), 6.23 (s, keto-CH), 3.85 (s, 3H, CH_3), 3.76 (s, 3H, CH_3O), and 2.36 ppm (s, CH_3); ^{13}C nmr (DMSO-d_6): δ 191.21 (ArCO), 181.90 (C-3), 163.90 (C-2), 149.29-123.54

(aromatic C), 116.35 (C-4), 99.44 (C-5), 57.37 ($2CH_3O$), and 22.89 ppm (CH_3). *Anal.* Calcd. for $C_{32}H_{29}N_3O_5$; C, 71.76; H, 5.46; N, 7.85. Found; C, 72.01; H, 5.77; N, 7.67.

5-(2-Aminophenyl)amino-3-hydroxy-4-(4-methoxylbenzoyl)-1-(4-methylphenyl)-5-(4-methoxyphenyl)-2,5-dihydro-2*H*-pyrrol-2-one (5c). 4-(4-Methoxybenzoyl)-5-(4-methoxyphenyl)-1-(4-methylphenyl)-1*H*-pyrrole-2,3-dione **1c** (1.0 g, 2.34 mmol) and *o*-phenylenediamine **4** (0.25 g, 2.34 mmol) were refluxed in benzene (50 mL) for 1 h. The solvent was evaporated and the remaining oily residue was treated with dry diethyl ether and stirred for 24 h. to give the yellow crude product which was recrystallized from *n*-butyl alcohol and allowed to dry on P_2O_5; resulting in yield 58% (0.73 g); mp 220-221°C; ir: 3615-3380 (br, NH and OH), 3360 (NH_2), 1716, 1680 (C=O); ^{1}H nmr (DMSO-d_6): δ 12.52 (br, -NH) , 9.79 (s, -NHO), 9.34 (s, enol-OH), 8.07-6.74 (m, 16H, Ar-H), 6.24 (s, keto-CH), 3.85 (s, 3H, CH_3), 3.74 (s, 3H, CH_3O), and 2.30 ppm (s, CH_3); ^{13}C nmr (DMSO-d_6): δ191.22 (ArCO), 181.75 (C-3), 163.91 (C-2), 149.16-121.95 (aromatic C), 115.77 (C-4), 99.53 (C-5), 57.35 ($2CH_3O$), and 22.90 ppm (CH_3). *Anal.* Calcd. for $C_{32}H_{29}N_3O_5$; C, 71.76; H, 5.46; N, 7.85. Found; C, 71.99; H, 5.57; N, 7.82.

5-(2-Aminophenyl)amino-3-hydroxy-4-(4-methoxylbenzoyl)-5-(4-methoxyphenyl)-1-(1-naphthyl)-2,5-dihydro-2*H*-pyrrol-2-one (5d). 4-(4-Methoxybenzoyl)-5-(4-methoxyphenyl)-1-(1-naphtyl)-2,3-1*H*-pyrrole-2,3-dione **1d** (1.0 g, 2.16 mmol) and *o*-phenylenediamine **4** (0.23 g, 2.16 mmol) were refluxed in benzene (50 mL) for 1 h. The solvent was evaporated and the remaining oily residue was treated with dry diethyl ether and stirred for 24 h. to give the yellow crude product which was recrystallized from *n*-butyl alcohol and allowed to dry on P_2O_5; resulting in yield 55% (0,68 g); mp 193°C; ir: 3610-3400 (br, NH and OH), 3260 (NH_2), 1715, 1675 (C=O); ^{1}H nmr (DMSO-d_6): δ12.66 (br, -NH) , 9.96 (s, -NHO), 9.82 (s, enol-OH), 8.19-6.75 (m, 19H, Ar-H), 6.29 (s, keto-CH), and 3.85 (s, 3H, CH_3), and 3.76 (s, 3H, CH_3O); ^{13}C nmr (DMSO-d_6): δ 191.28 (ArCO), 179.81 (C-3), 163.87 (C-2), 147.22-121.55 (aromatic C), 115.34 (C-4), 99.52 (C-5), 57.35 ($2CH_3O$). *Anal.* Calcd. for $C_{35}H_{29}N_3O_5$; C, 73.54; H, 5.11; N, 7.35. Found; C, 73.25; H, 5.11; N, 7.17.

3-[1-(4-Methoxylbenzoyl)-2-(4-methoxylphenyl)-2-phenylaminovinyl]-1*H*-quinoxalin-2-one (6a). 4-(4-Methoxybenzoyl)-5-(4-methoxyphenyl)-1-phenyl-2,3-1*H*-pyrrole-2,3-dione **1a** (1.0 g, 2.42 mmol) and *o*-phenylenediamine **4** (0.26 g, 2.42 mmol) were stirred in benzene (50 mL) at 25°C for 24 h. The orange crystaline product was filtered and recrystallized from benzene and allowed to dry on P_2O_5; resulting in yield 69% (0,84 g); mp 159-160°C; ir: 3400-3250 (NH), 1670, (C=O), 1610 (C=O); ^{1}H nmr (DMSO-d_6): δ 12.40 and 11.90 (-NH), 8.21-7.19 (m, 17H, Ar-H), 6.25 (s, C-H), and 3.84 (s, 3H, CH_3O), and 3.67 ppm (s, 3H, CH_3O); ^{13}C nmr (DMSO-d_6): δ195.98 (ArCO), 158.01 (lactam C), 155.51 (C-3), 134.01-115.02 (aromatic C), and 57.01 and 56.24 ppm ($2CH_3O$). *Anal.* Calcd. for $C_{31}H_{25}N_3O_4$; C, 73.94; H, 5.00; N, 8.34. Found; C, 73.57; H, 4.73; N, 8.07.

3-[1-(4-Methoxylbenzoyl)-2-(4-methoxylphenyl)-2-*o*-tolylaminovinyl]-1*H*-quinoxalin-2-one (6b). 4-(4-Methoxybenzoyl)-5-(4-methoxyphenyl)-1-(2-methylphenyl)-1*H*-pyrrole-2,3-dione **1b** (1.0 g, 2.34 mmol) and *o*-phenylenediamine **4** (0.26 g, 2.34 mmol) were stirred in benzene (50 mL) at 25°C for 24 h. The orange crystaline product was filtered and recrystallized from benzene and allowed to dry on P_2O_5; resulting in yield 73% (0.88 g); mp 165-166°C; ir: 3300-3230 (NH), 1690, (C=O), 1630 (C=O); ^{1}H nmr (DMSO-d_6): δ 12.51 and 12.10 (-NH), 7.89-7.05 (m, 16H, Ar-H), 6.84 (s, C-H), 3.78 (s, 3H, CH_3O), 3.53 (s, 3H, CH_3O), and 2.52 ppm (s, CH_3); ^{13}C nmr (DMSO-d_6): δ196.52 (ArCO), 158.55 (lactam C), 156.72 (C-3), 134.05-114.88 (aromatic C), 57.23 and 56.99 ($2CH_3O$) and 20.67 ppm (CH_3). *Anal.* Calcd. for $C_{32}H_{27}N_3O_4$; C, 74.26; H, 5.26; N, 8.12. Found; C, 74.54; H, 5.50; N, 7.82.

3-[1-(4-Methoxylbenzoyl)-2-(4-methoxylphenyl)-2-*p*-tolylaminovinyl]-1*H*-quinoxalin-2-one (6c). 4-(4-Methoxybenzoyl)-5-(4-methoxyphenyl)-1-(4-methylphenyl)-1*H*-pyrrole-2,3-dione **1c** (1.0 g, 2.34 mmol) and *o*-phenylenediamine **4** (0.25 g, 2.34 mmol) were stirred in benzene (50 mL) at 25°C for 24 h. The orange crystaline product was filtered and recrystallized from benzene and allowed to dry on P_2O_5; resulting in yield 70% (0.85 g); mp 152-153°C; ir: 3450-3208 (NH), 1685, (C=O), 1648 (C=O); ^{1}H nmr (DMSO-d_6): δ 12.44 and 12.01 (-NH), 7.88-7.11 (m, 16H, Ar-H), 6.32 (s, C-H), 3.78 (s, 3H, CH_3O), 3.69 (s, 3H, CH_3O), and 2.23 ppm (s, CH_3); ^{13}C nmr (DMSO-d_6): δ 196.53 (ArCO), 158.51 (lactam C), 156.42 (C-3), 134.11-114.89 (aromatic C), 57.22 and 57.02 ($2CH_3O$) and 20.55 ppm (CH3). *Anal.* Calcd. for $C_{32}H_{27}N_3O_4$; C, 74.26; H, 5.26; N, 8.12. Found; C, 74.61; H, 5.41; N, 7.87.

3-[1-(4-Methoxylbenzoyl)-2-(4-methoxylphenyl)-2-naphthylaminovinyl]-1*H*-quinoxalin-2-one (6d). 4-(4-Methoxybenzoyl)-5-(4-methoxyphenyl)-1-(1-naphtyl)-2,3-1*H*-pyrrole-2,3-dione **1d** (1.0 g, 2.16 mmol) and *o*-phenylenediamine **4** (0.25 g, 2.34 mmol) were stirred in benzene (50 mL) at 25°C for 24 h. The orange crystaline product was filtered and recrystallized from benzene and allowed to dry on P_2O_5; resulting in yield 65% (0.77 g); mp 209°C; ir: 3500-3250 (NH), 1680, (C=O), 1625 (C=O); ^{1}H nmr (DMSO-d_6): δ 12.07 (-NH), 8.41-6.91 (m, 19H, Ar-H), 6.74 (s, C-H) and 3.83 (s, 3H, CH_3O), and 3.59 ppm (s, 3H, CH_3O); ^{13}C nmr (DMSO-d_6): δ 194.73 (ArCO), 158.97 (lactam C), 155.98 (C-3), 133.01-115.07 (aromatic C), and 56.99 and 54.65 ppm ($2CH_3O$). *Anal.* Calcd. for $C_{35}H_{27}N_3O_4$; C, 75.93; H, 4.92; N, 7.59. Found; C, 75.93; H, 4.75; N, 7.56.

4-(4-Methoxylphenyl)[2-(4-methoxylphenyl)furo[2,3-*b*]-quinoxalin-3-yl]methanone (7). Compounds of **6a-d** (1 g, 2.34 mmol) were heated until they were dissolved in *n*-butyl alcohol and kept at 25 °C for 24 h. The yellow product was filtered and allowed to dry on P_2O_5; resulting in yield 47% (0.45 g); mp 235-236°C; ir: 1650 (C=O); ^{1}H nmr (DMSO-d_6): δ 8.16-6.90 (m, 12H, Ar-H), 3.87 (s, 3H, CH_3O), and 3.65 ppm (s, 3H, CH_3O); ^{13}C nmr (DMSO-d_6): δ 189.80 (ArCO), 172.68 (N-C=O), 167.81 (C1=O), 137.54 (Ar-C3-OH, in enol form) 134.15-114.98 (aromatic C), and 56.24 ppm ($2CH_3O$). *Anal.* Calcd. for $C_{25}H_{18}N_2O_4$; C, 73.17; H, 4.39; N, 6.83. Found; C, 73.31; H, 4.67; N, 6.99.

Acknowledgement. This project was financially supported by the Science and Technical Research Council of Turkey (TÜBİTAK, project no:**TBAG-AY/118**), Resarch Center of Erciyes University. Authors want to express their gratitude to D. Unal and Dr. S. Patat.

REFERENCES

** To whom correspondence should be addressed.

[1a] Kollenz, G.; Ott, W.; Ziegler, E.; Peters, K.; von Schnering, H.G.; Quast, H. *Liebigs Ann. Chem.*, 1980 1801; [b] Kollenz, G.; Ott, W.; Ziegler, E.; Peters, K.; von Schnering, H.G.; Formacek, V.; Quast, H. *Liebigs Ann. Chem.*, 1984 1137.

[2a] Peters, K.; Kollenz, G. *Chem., Ber.*, 1981, *114*, 1206; [b] Kollenz, G.; Penn, G.; Dolenz, G.; Akçamur, Y.; Peters, K.; Peters, E.-

M.; von Schnering, H. G. *Chem. Ber.,* 1984, *117*, 1299; [c] El-Nabi, H. A.; Kollenz, G. *Monatsh. Chem.,* 1997, *128*, 381.

[3a] Kollenz, G.; Penn, G.; Ott, W.; Peters, K.; Peters, E.-M.; von Schnering, H. G. *Chem.Ber.,* 1984, *117*, 1310; [b] Heilmayer, W.; Kappe, C. O.; Sterk, H.; Kollenz, G.; Peters, K.; Peters, E.-M.; von Schnering H. G.; Walz, L. *Chem.Ber.,* 1993, *126*, 2061.

[4] Kollenz, G.; Penn, G.; Ott, W.; Peters, K.; Peters, E.-M.; von Schnering, H. G. *Heterocycles,* 1987, *26*, 625.

[5] Terpetschnig, E.; Penn, G.; Kollenz, G.; Peters, K.; Peters, E.-M.; von Schnering, H. G. *Tetrahedron,* 1991, *47,* 3045.

[6a] Ott, W. *Synthesis*, 1976 478; [b] Ott, W.; Terpetschnig, E.; Sterk, H.; Kollenz, G. *Synthesis*, 1987 176.

[7] Kollenz, G.; Terpetschnig, E.; Sterk, H.; Peters, K.; Peters, E.-M. *Tetrahedron,* 1999, *55,* 2973.

[8a] Cappe, C. O.; Kollenz, G.; Wentrup, C. *J. Chem. Commun*., 1992 485; [b] Cappe, C. O.; Kollenz, G.; Leung-Toung, R.; Wentrup, C. *J. Chem. Commun*., 1992, 488.

[9a] Kost, A. N.; Grandberg, I. I. *Adv. Heterocyclic Chem.,* 1966, *6*, 347; [b] Sammes, M. P.; Katritzky, A. R. *Adv. Heterocyclic Chem.,* 1983, *34*, 1; [c] Elguero, J. in Comprehensive Heterocyclic Chem., Vol 4, Katritzky, A. R.; Rees, C. W. Eds, Pergamon Press, Oxford, 1984, Chapter 4,4; [d] Theobald, R. S. in: Coffey S.; Ansell, M. F. (Eds.), Rodd's Chemistry of Carbon Compounds, 2nd Edn., Vol IV^{c}, Elsevier Science Publishers, Amsterdam, p 1 (1986). [e] Elnagdi, M. H.; Elgemeie, G. E. H.; Abd-Elmaksoud, F. A. E. *Heterocycles,* 1985, *23*, 3121; [f] Mullins, S. T. in: Coffey S.; Ansell, M. F. (Eds.), Rodd's Chemistry of Carbon Compounds, Suppl. of Vol IV$^{c/d}$, Elsevier Science Publishers, Amsterdam, p 1 (1994).

[10a] Knorr, L. *Ber*., 1884, *17*, 549; [b] Heming, A. E.; Kuzell, W. C. *Antibiot. Chemother*., 1953, *3*, 634; [c] Hermann, E.; Gabliks, J. *Cancer Chemother. Rept*., 1961, *14*, 85; [d] Ha, H. J.; Oh, S. J.; Lee, S. K.; Song, C. E. *Korean J. Med. Chem*., 1996, 6; [e] Maggio, B.; Daidone, G.; Rafa, D.;Plescia, S.; Mantione, L.; Cutuli, V. M. C.; Mangano, N. G.; Eur Caruso, A. *J. Med. Chem*., 2001, *36*, 737.

[11a] Hanson, G. A. *Bull. Soc. Chim. Belg.,* 1958, *67*, 707; [b] Neunhoeffer, O.; Alsdorf, G.; Ulrich, H. *Chem. Ber.,* 1959, *92*, 252; [c] Baroni, E. E.; Kovyrzina, K. A. *Zh. Obshch. Khim.,* 1961, *31*, 1641.

[12] Brock, E. D.; Lewis, D. M.; Yousaf, T. I.; Harper, H. H. PCT Int. Appl. 1999 pp. 44.

[13a] O'Brien, D.; Weaver, M. S.; Lidzey, D. G.; Bradley, D. D. C. *Appl. Phys. Lett.,* 1996, *69*, 881; [b] Dailey, S.; Feast, W. J.; Peace, R. J.; Sage, I. C.; Till, S.; Wood, E. L. *J. Mater. Chem.,* 2001, *11*, 2238.

[14a] Cheeseman G. W. H.; Cookson, R. F. ed. by Weissberger, A.; Taylor, E. C. *The Chemistry of Heterocyclic Compounds,* Vol. 35, Wiley, J.; Sons, New York, 1979, pp. 1–27, 35-38; [b] Porter, A. E. A. *Comprehensive Heterocyclic Chemistry,* 1984, Vol. 3, ed. by Katrizky A. R.; Rees, C. W. Pergamon, New York, pp.157–197; [c] Gazit, A.; App, H.; McMahon, G.; Chen, J.; Levitzki, A.; Bohmer, F. D. *J. Med. Chem.,* 1996, *39*, 2170; [d] Sehlstedt, U.; Aich, P.; Bergman, J.; Vallberg, H.; Norden, B.; Graslund, A. *J. Mol. Biol.,* 1998, *278*, 31.

[15a] Musatova, I. S.; Elina, A. S.; Padeiskaya, E. N.; Shipilova, L. D.; Yakobson, G. G.; Furin, G. G. *Khim. Farm. Zh*., 1982, *16*, 934; [b] Musatova, I. S.; Elina, A. S.; Padeiskaya, E. N. *Khim. Farm. Zh.,* 1982, *16*, 1063; [c] Monge, A.; Gil, M. J.; Pascual M. A.; Gastelurrutia, M. A. *An. R. Acad. Farm.,* 1983, *49*, 37 ; *Chem. Abstr.,* 1983, *99***,** 194924s,; [d] Monge, A.; Gil, M. J.; Pascual, M. A. *An. R. Acad. Farm.,* 1983, *49*, 199.

[16] Ganley, B.; Chowdhury, G.; Bhansali, J.; Daniels, J. S.; Gates K. S. *Bioorg. Med. Chem.,* 2001, *9*, 2395.

[17a] Ziegler, E.; Eder, M.; Belegratis, K.; Prewedourakis, E. *Monatsh. Chem.,* 1967, *98*, 2249; [b] Kollenz, G.; Kappe, C. O.; El Nabey, H. A. *Heterocycles,* 1991, *32*, 669; [c] Saalfrank, R. W.; Lutz, T.; Hörner, B.; Gündel, J.; Peters, K.; von Schnering, H. G. *Chem. Ber.,* 1991, *124*, 2289; [d] Sarıpınar, E.; Güzel, Y.; Önal, Z.; İlhan, İ. Ö. Akçamur, Y. *J. Chem., Soc., Pak.,* 2000, *22*, 308.

[18] Sarıpınar, E.; Karataş, S. *J. Heterocyclic Chem*., 2005, *42*, 787.

[19a] Yıldırım, İ.; Sarıpınar, E.; Güzel, Y.; Patat, Ş.; Akçamur, Y. *J. Mol. Struct., (Theochem),* 1995, *334*, 165; [b] Şener, A.; Kasımoğulları, R.; Şener, M. K.; Bıldırıcı, İ.; Akçamur, Y. *J. Heterocyclic Chem.,* 2002, *39*, 869; [c] Kappe, C. O.; Terpetschnig, E.; Penn, G.; Kollenz, G.; Peters, K.; Peters, E. M.; von Schnering, H. G. *Liebigs Ann*., 1995, 537; [d] İlhan, İ. Ö.; Sarıpınar, E.; Akçamur, Y. *J. Heterocyclic Chem*., 2005, *42*, 117.

[20a] Ott, W.; Ziegler, E.; Kollenz, G. *Synthesis*, 1976, *7*, 477; [b] Kollenz, G.; Kriwetz, G.; Ott, W.; Ziegler, E. *Liebigs Ann. Chem*., 1977 1964; [c] Sarıpınar, E.; Saglam, E. G.; Oncel, İ.; İlhan, İ. Ö.; Goktaş, L.; Kok, T. R.; Akcamur, Y. *Heterocycles*, 2005, *65*, 2161.