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4-(4-Methylbenzoyl)-5-(4-methylphenyl)furan-2,3-dione: Synthesis, Thermolysis and Reactions with Aromatic Amines and Diamines

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The 1,3-dicarbonyl compounds, *e.g.*, *p,p'*-dimethyldibenzoylmethane (**1**) combines with oxalyl chloride to yield 4-(4-methylbenzoyl)-5-(4-methylphenyl)furan-2,3-dione (**2**) which is a novel starting material for synthesizing many heterocyclic compounds. Thermal decomposition of **2** is supposed to occur by the ring opening of the compound **2** followed by the intermediate diacylketene dimerization resulting in the pyran-4-one (**3**). The reactions of **2** with α-naphthylamine, aniline, *p*-toluidine, *o*-toluidine or *o*-phenylenediamine derivatives in benzene at the room temperature led to the formation of the 2-oxo-3-butenoic acid derivative (**4**), the pyrrol-2,3-dione (**5**), the pyrrole-2-ones (**6**), and the quinoxaline-2-ones (**7**) derivatives, respectively. All new synthesized compounds were characterized by elemental analysis, IR, ^{1}H and ^{13}C NMR spectral data. Most of them were compared with their previous analogues.

Key Words: 2,3-Furandione, Furan-2,3-dione, Pyrrole-2-one, Pyrrol-2,3-dione, Quinoxaline-2-one, Cyclocondensation, Michael type addition.

INTRODUCTION

2,3-Furandiones, belong to an important group of heterocyclic starting compounds, have been the subject of extensive study in the recent past. Due to their high reactivity, numerous reports have highlighted their chemistry[1]. The cyclocondensation reaction of 1,3-dicarbonyl compounds with oxalic acid or its derivatives, *e.g.*, oxalyl chloride representing a convenient synthesis of furan-2,3-dione systems yields γ-lactones[2]. In furan-2,3-diones carbon atoms C-2, C-3, C-5 and C-6 represent electrophilic sites of different reactivity and could be used for the construction of condensed heterocyclic systems upon reaction with various nucleophiles and binucleophiles[3]. The reactions of substituted 2,3-furandiones with some dienophiles in different solvents and at various temperatures have also been studied[4]. A convenient method for the synthesis and the mechanism of

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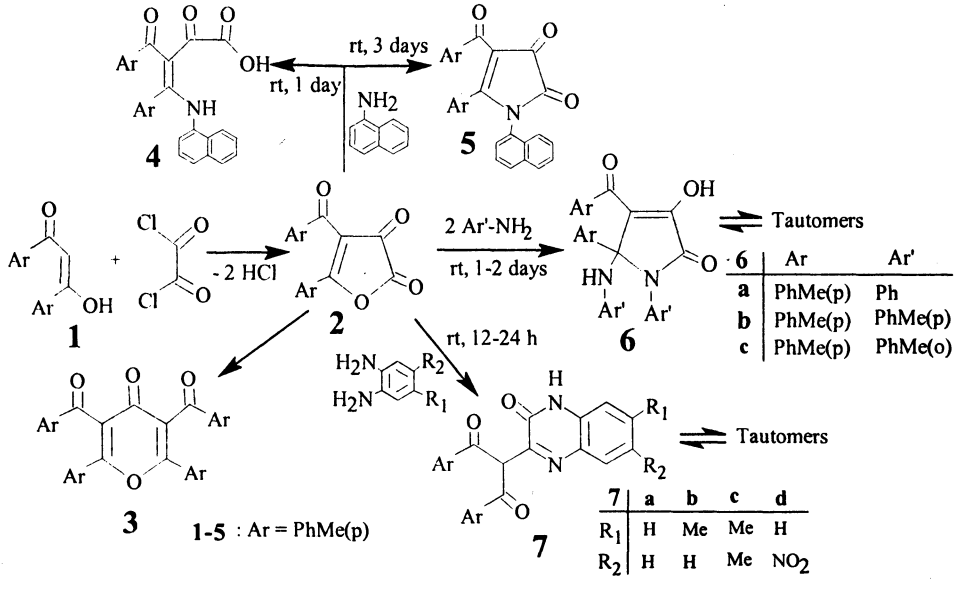
reactions and calculations on the interaction of 2,3-dihydro-2,3-furandiones with several semicarbazones, ureas and their thio-analogues have been reported recently[5]. The reactions are generally initiated by the nucleophilic attack of the nitrogen atom of semicarbazone or urea, directed on to the oxygen atom of the furan ring. Thermal decomposition of the 2,3-furandiones leads to the formation of α-oxoketene intermediates[6]. These acylketenes are highly reactive molecules which can be trapped by nucleophiles to give β-ketocarboxylic acid derivatives[7] or alternatively undergo cycloaddition reactions[8]. The general reactivity of ketenes and the mechanism of the reactions with nucleophiles have been reviewed recently, and a few *ab initio* and semi-empirical (AM1 and PM3) calculations on a series of differently substituted α-oxoketenes, especially substituent effects on their stability as well as reactivity, have been published[9].

For this reason the aim of this study was to synthesize a novel 4(4-methylbenzoyl)-5-(4-methylphenyl)furan-2,3-dione **(2)** to make notable contributions to new heterocyclic compounds that are in general well known for their potential biological activities[3f]. We report the synthesis and characterization of the titled compound **2** using the synthetic procedure based on the ring closure reaction of *p,p'*-dimethyldibenzoylmethane **(1)** with oxalyl chloride, our findings during the course of synthesizing **2** (see **Scheme-1**), too, as well as further investigations of its thermal decomposition and reactivity with some aromatic amines and diamines at various temperatures and in different solvents. Therefore, we also synthesized the compounds pyran-4-one **(3)**, 2-oxo-3-butenoic acid **(4)**, pyrrol-2,3-diones **(5, 6)** and quinoxalin-2-ones **(7)** derivatives by conventional chemical procedures. The compound **(2)** which includes *p*-methyl groups in its



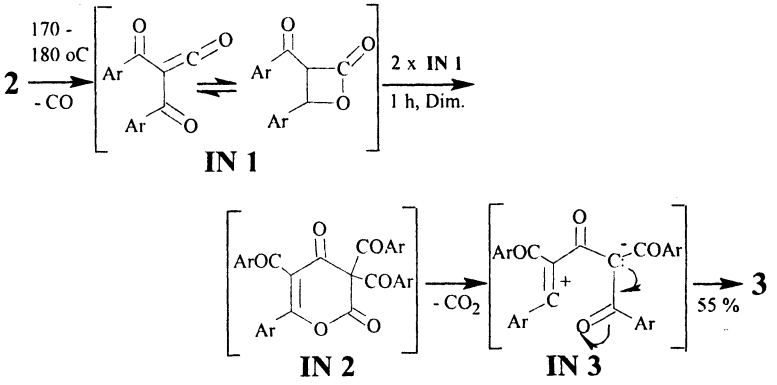
Scheme-1

structure, is a new compound synthesized in our laboratories by us and have been used as the substrate (**Scheme 1**).

RESULTS AND DISCUSSIONS

It is well known that active methylenes of the 1,3-diones similar to the compound **1**, obtained easily from $NaOCH_3$ and 2,3-dibromo-1,3-bis(4-methylphenyl)-1-propanone, react with oxalyl halides in the presence of base[2]. Thus, treatment of 1,3-bis(4-methylphenyl)propane-1,3-dione with oxalyl chloride in boiling benzene gave 4-(4-methylbenzoyl)-5-(4-methylphenyl)-2,3-dihydro-2,3-furandione (**2**) as pale yellow needles in 80–85% yield. The structure of **2** was confirmed beside elemental analysis by IR, ^1H and ^{13}C NMR spectroscopic techniques that supported the structure (**Scheme-1**). These results are in good agreement with a similar finding with substituted 2,3-dihydro-2,3-furandiones[1, 2, 6a]. The formation of **2** was supported by the results of spectroscopic measurements particularly in the presence of three carbonyl characteristic absorption bands (FT-IR: 1826, 1731, 1642 cm^{-1}). The ^1H NMR spectrum of **2** showed a singlet 2.38 ppm for CH_3 groups, and two multiplet between 6.81–7.90 ppm for aromatic protons, respectively. Final confirmation of structure **2** was derived from its ^{13}C NMR spectrum: 190.35 (t, J = 4.0 Hz, C_6 = O), 187.40 (C_3=O), 178.59 (t, J = 4.2 Hz, C_5), 177.87 (C_2=O) and 118.08 ppm (C_4).

Thermolysis of **2** at 170–180°C resulted in CO extrusion and formation of the intermediate diacylketene (**IN1, Scheme 2**)[1b, 6c]. Little is known about four-membered heterocycles, in general, and the possible acylketene/oxetone valence tautomerization, in particular. However, the oxetone possesses the additional feature that resonance of the carbonyl groups leads to formally anti-aromatic structure. Hence, oxetone tautomer is thermodynamically less stable than diacylketene form[9b, d]. A reasonable proposal different from that discussed with thermolysis[10] for reaction pathway from furandione **2** to γ-pyrone **3** is outlined briefly in **Scheme-2.**

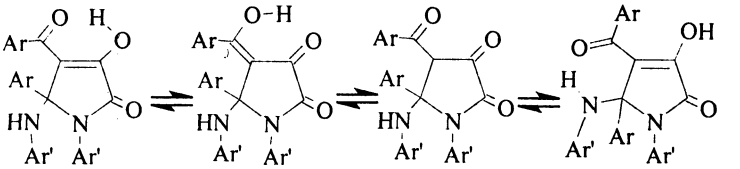


Scheme-2

In the absence of nucleophiles or suitable dienophiles, dimerization of acylketenes takes place as a special case of hetero-*Diels-Alder* cycloaddition reactions[6b, 11]. In these reactions the acylketene, generally, dimerizes to the pyran-2,4-dione derivative **(IN2)** under ordinary reaction conditions in a process involving a [4 + 2] cycloaddition of one ketene molecule to the (C=C) double bond of another molecule, and gives pyran-4-one **3** as final stable compound on the molecule CO_2 disconnection. The dimerization proceeds *via* a transition state by approach of the two acylketene molecules occurring rather unsymmetrically. The structure of γ-pyrone **3** is confirmed by its characteristic IR and ^{13}C NMR spectroscopic data: three carbonyl absorption bands (ν = 1675, 1637 cm^{-1}) as well as the corresponding signals in the ^{13}C NMR spectrum (δ = 194.64, 178.12, 164.07, 127.01 ppm).

The compound **2** reacts with 1-naphthylamine in two ways yielding the 2-oxo-3-butenoic acid derivative **4** and the 2,3-pyrroledione derivative **5** similarly reported previously[3a]. At the room temperature in benzene, mixing of furandione **(2)** and corresponding amine (1 : 1 mol) about 1 day and 3 days led to the formation of the novel compounds **4** and **5** in approximately 56% and 75% yields, respectively **(Scheme-1)**. The moderate to excellent yields of the reactions can be explained by the chemical behaviour of furandiones similar to the compound **2** towards H-active nucleophiles[3b, 6a, f]. Addition of nucleophiles to the furandiones usually starts with nucleophilic attack at one of the C-2, C-3 and C-5 positions of the furan ring system[3e, 5]. The formation of the 2,3-pyrroledione **(5)** may be viewed as occurring *via* a Michael type addition to C-5 atom of **2**, a very similar attack of other nucleophiles on the furandione analogues of **2** was discussed in many previous papers[3, 4, 5]. Compound **5** showed characteristic IR absorption bands at 1757 (s), 1713 (vs, lactam carbonyl) and 1649 (s) cm^{-1}, typical of 2,3-pyrrolediones[12]. The ^{13}C NMR signals of **5** appeared at 190.21 (t, J = 4.3 Hz, C-6), 181.12 (C-3), 174.84 (t, J = 4.6 Hz, C-5), 160.21 (C-2) and 115.01 (C-4). Further confirmation also came from ^1H NMR data. Comparison of the IR and NMR spectroscopic data of **5** among themselves and with those of several analogues reported in[3a, b, 6f, 12], together with correct results of its elemental analysis, evidence its molecular skeleton.

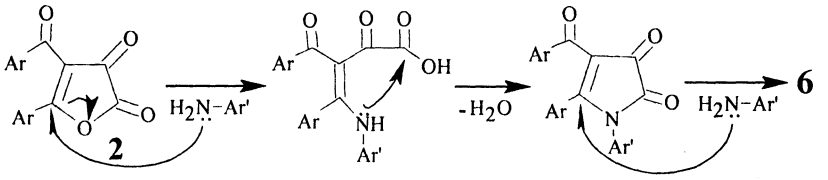
Interaction of **2** with corresponding aromatic amines led to form the derivatives of 2-pyrrolone **(6)** which have tautomeric forms **(Chart 1)**. Furandione **(2)** reacts



6

Chart-1

with two moles aniline, *p*-toluidine or *o*-toluidine yielding the 2-pyrrolones **(6a–c),** which on the other hand are synthesized by nucleophilic Michael addition at C-5 of corresponding aromatic amines to the 2,3-pyrrolediones[3a, 12b]. The reactions proceeded smoothly at room temperature in benzene for 1–2 d and afforded the corresponding 2-pyrrolone derivatives **6** in yields (60–80%). The primary nucleophilic attack of the amino groups of amine to open the furandione ring in **2** obviously occurs again at C-5 (**Scheme-3**) as observed with several other



Scheme-3

nucleophiles[3c, 4d]. However, the compounds of type **6** could not obtain from experimentations of the naphthylamine with furandione **(2)** (2 : 1 mol). This event can be explained with steric hindrance of naphthyl group.

The ^{13}C NMR spectrum of **6c** exhibits two signals at $\delta = 164.40$ (C-2) and 181.01 (C-3) for the two vicinal carbonyl carbon atoms and a signal of the sp^3 ring carbon (C-5) at 91.50 ppm. These chemical shift values are in good agreement with the proposed 2,3-pyrroledione structure[12, 13] **(6c)** and confirm that the "oxalyl moiety" (C-2 and C-3) was not attacked by the amine nucleophile.

Nucleophilic addition of *o*-phenylenediamine and its derivatives to furandione **(2)** provided quinoxalin-2-ones **(7a–d)** in 47–68% yields. All reactions were carried out at room temperature in inert solvents[3b, 6c]. These products arise from the sequential attacks of aromatic diamines at the C-3 and C-2 atoms of the furandione **2**, respectively, followed by elimination of water and furan ring opening. Therefore, presence of tautomeric forms of **7**, as well as the stability of the compounds of type **7** was also confirmed by these reactions, outlined briefly in **Scheme 1** and **Chart 2.** The ^{13}C NMR spectrum of **7c** exhibits significant line broadenings for the carbons C-10, C-10′ (aroyl carbonyls = 195.43 ppm), C-3 (157.96 ppm), C-2 (155.61 ppm) and C-9 (d, $J_{CH} = 139$ Hz, 60.78 ppm), respectively. In the IR spectrum of **7c**, characteristic absorption bands at about 3443 (b) cm^{-1} (NH ⇌ OH), 1694 (s) (C=O) and 1659 (vs) (C=O) were observed, as well as, the ^1H NMR spectrum of **7c** shows that (NH ⇌ OH) proton appears at $\delta = 12.55$ ppm, respectively, thus indicating a rapid and intense exchange process among several tautomeric species. Other spectral and analytical data of **7a-d** are in full agreement with their proposed structures as well.

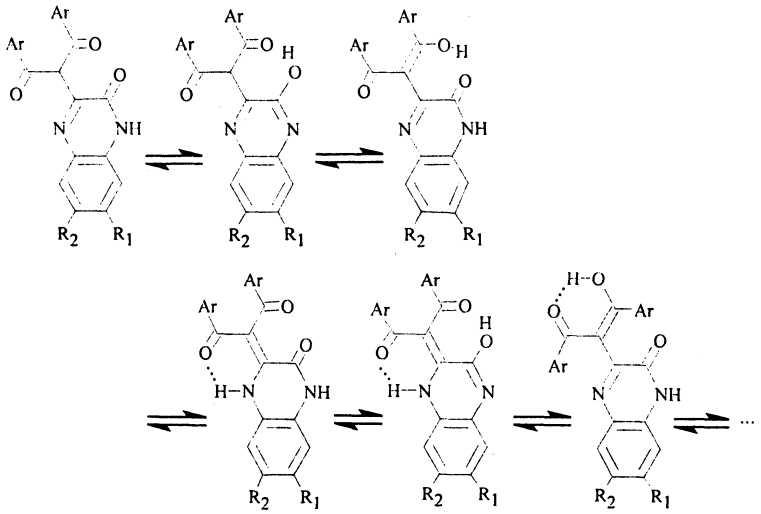


Chart-2

EXPERIMENTAL

Solvents were dried by refluxing with 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 analyzer model 1108. The IR spectra were recorded on a Jasco FT-IR spectrometer model 460, using KBr pellets. The ^{1}H and ^{13}C NMR spectra were obtained on Varian Gemini 200 instrument with TMS as internal standard. All experiments were followed by TLC using DC Alufolien Kieselgel 60 F_{254} Merck and Camag TLC lamp (254/366 nm).

***p,p'*-Dimethyldibenzoylmethane (1):** To a solution of NaOH (22 g) in a mixture of ethanol (140 mL) and water (200 mL) were added *p*-methylacetophenone (67.0 mL) dropwise with stirring at room temperature. *p*-Methylbenzaldehyde (58.8 mL) was poured into the mixture and stirred for 5 h and then kept in a fridge for a night. The crude precipitate was filtered off and washed with ethanol solution and dried to yield 116.0 g (96%) of pure *p,p'*-dimethylbenzalacetophenone. Then, to the solution of *p,p'*-dimethylbenzal-acetophenone (11.53 g, 0.05 mol) in carbon tetrachloride (150 mL) was added bromine (7.8 g, 0.05 mol) dropwise with stirring about –10°C for 2 h. After filtering the orange crude product, it was washed in cold and warm alcohols, respectively, and dried to afford 9.23 g (60 %). To a solution of 2,3-dibromo-1,3-bis(4-methylphenyl)-1-propanone (20 g, 0.05 mol) in methanol (50 mL) was added $NaOCH_3$, which was prepared by dissolving small pieces of natrium (2.32 g) in dry methanol (40 mL) stirred for 1 h at 50–60°C. After cooling to room temperature, the solution was acidified by adding Conc. HCl (pH = 1). The precipitate was kept in a refrigerator for 1 h, filtered off and washed with water

and recrystallized from methanol to give 1.62 g (51%) pure 1,3-bis(4-methylphenyl)propane-1,3-dione (*p,p'*-dimethyldibenzoylmethane) **(1)**, m.p.: 122°C; IR (cm^{-1}) (KBr): 3060–2900 ν(aromatic and aliphatic C—H stretching, respectively), 2850 (enolic O—H stretching[14]), 1612, 1609 ν(C=O); ^1H NMR ($CDCl_3$, δ): 7.94–7.21 (two m, 8H, Ar—H), 6.83 (enolic O—H), 4.59, 3.50 (weak piks, tautomeric protons), 2.42, 241 ppm (s, 6H, CH_3); ^{13}C NMR ($CDCl_3$, δ): 187.47 (Ar—C=O), 145.16, 134.85, 131.42, 129.21 (aromatic carbons), 94.45 (s, enolic =CH—, C-2), 23.65 ppm (s, CH_3). Elemental analysis: found (calcd.): [C = 81.09 (80.93), H = 6.33 (6.39)].

4-(4-Methylbenzoyl)-5-(4-methylphenyl)furan-2,3-dione (2): *p, p'*-Dimethyldibenzoylmethane (1.0 g, 3.96 mmol) and oxalyl chloride (0.4 mL, 4.66 mmol) were refluxed in dry benzene for 50–60 min. The solvent was evaporated and the remaining oily residue was treated with petroleum ether (40–60°C) for 2 h to give a yellow precipitate which was filtered off and washed with dry petroleum ether for several times; yield 1.0 g (82%), m.p. 95°C; IR (cm^{-1}) (KBr): 1826, 1731, 1642 ν(C=O); ^1H NMR ($CDCl_3$, δ): 7.90–6.81 (two m, 8H, Ar—H), 2.38 ppm (s, 6H, CH_3); ^{13}C NMR ($CDCl_3$, δ): 190.35 (t, J = 4.0 Hz, Ar—C=O), 187.40 (s, C-3), 178.59 (t, J = 4.2 Hz, C-5), 177.87 (s, C-2), 149.93, 148.13, 145.21, 135.45, 134.75, 132.20, 131.92, 131.84, 131.77, 131.41, 129.20, 124.75 (aromatic carbons), 118.08 (s, C-4), 24.15 (s, CH_3 23.64 ppm (s, CH_3). Elemental analysis: found (calcd.): [C = 74.38 (74.50), H = 4.84 (4.61)].

3,5-Di-*p*-methylbenzoyl-2,6-di-*p*-tolyl-4*H*-pyran-4-one (3): Compound **2** (0.50 g, 1.63 mmol) was heated to 170–180°C for 30–40 min. White crystals of **3** (0.23 g, 55%) were obtained by filtering, after cooling the residue to the room temperature, triturating with ether and recrystallization from *n*-butanol; m.p. 247°C; IR (cm^{-1}) (KBr): 1675 ν(C_4=O), 1637 ν(Ar—C=O), 1600–1430 ν(C···C, aromatic rings); ^1H NMR ($CDCl_3$, δ): 7.91–7.17 (m, 16H, Ar—H), 2.38, 2.36 ppm (s, 12H, CH_3); ^{13}C NMR ($CDCl_3$, δ): 194.64 (t, J = 3.9 Hz, Ar—C=O), 178.12 (s, C-4), 164.07 (t, J = 2.8 Hz, C-2), 127.62 (s, C-3), 146.96–130.12 (aromatic carbons), 23.80 (s, CH_3), 23.51 ppm (s, CH_3). Elemental analysis: found (calcd.): [C = 82.26 (82.01), H = 5.67 (5.51)].

3-*p*-Methylbenzoyl-4-(1-naphthylamino)-4-*p*-tolyl-2-oxo-3-butenoic acid (4): An equimolar mixture of the compound **2** (0.50 g, 1.63 mmol) and 1-naphthylamine (0.24 g, 1.67 mmol) was dissolved in toluene (approximately 30 mL) and stirred at room temperature for 24 h. After the white precipitate was obtained by suction filtration, it was carefully washed with ether several times and dried to afford 0.41 g (56%) of **4**, m.p.: 147°C; IR (cm^{-1}) (KBr): 3254 ν(br, NH and OH), 1776 ν(s, C=O), 1671 ν(m, C=O), 1620, 1581, 1562, 1516, 1483 ν(C···C, C···N); ^1H NMR (d_6-DMSO, δ): 11.02 (s, 1H, OH), 10.84 (s, 1H, NH), 8.45–6.88 (m, 15H, Ar—H), 2.38 (s, 3H, CH_3), 2.09 ppm (s, 3H, CH_3); ^{13}C NMR (d_6-DMSO, δ): 190.19 (t, J = 4.0 Hz, Ar—C=O), 186.81 (s, C-2), 181.11 (s, C-1), 174.83 (t, J = 4.3 Hz, C-4), 160.21 (s, N-Ph), 145.51–115.01 (aromatic carbons),

94.32 (s, C-3), 23.00 (s, CH_3), 22.69 ppm (s, CH_3). Elemental analysis: found (calcd.): [C = 77.51 (77.49), H = 5.17 (5.16), N = 3.37 (3.12)].

1-α-Naphthyl-4-*p*-methylbenzoyl-5-*p*-tolyl-1*H*-pyrrole-2,3-dione (5): An equimolar mixture of the compound **2** (0.50 g, 1.63 mmol) and 1-naphthylamine (0.24 g, 1.67 mmol) was dissolved in benzene (approximately 30 mL) and stirred at room temperature for 72 h. After the deep red precipitate was obtained by suction filtration, it was carefully washed with ether several times and dried to afford 0.53 g (75%) of **5,** m.p.: 227°C; IR (cm^{-1}) (KBr): 1757, 1713, 1649 ν(s, C=O), 1605–1507 ν(C···C, C···N, aromatic rings); ^1H NMR (d_6-DMSO, δ): 8.46–6.87 (m, 15H, Ar—H), 2.37 (s, 3H, CH_3), 2.08 ppm (s, 3H, CH_3); ^{13}C NMR (d_6-DMSO, δ): 190.21 (t, J = 4.3 Hz, Ar—C=O), 181.12 (s, C-3), 174.84 (t, J = 4.6 Hz, C-5), 160.21 (s, C-2), 115.01 (s, C-4), 145.51–125.40 (aromatic carbons), 23.03 (s, CH_3), 22.69 ppm (s, CH_3). Elemental analysis: found (calcd.): [C = 80.53 (80.72), H = 5.01 (4.91), N = 3.17 (3.25)].

3-Hydroxy-4-*p*-methyl benzoyl-1-phenyl-5-phenyl amino-5-*p*-tolyl-1,5-dihydro-2*H*-pyrrol-2-one (6a): To a solution of the compound **2** (0.50 g, 1.63 mmol) in benzene (40 mL) aniline (0.30 mL, 3.26 mmol) was added dropwise. After the reaction mixture had been stirred at room temperature for 2–3 days the yellow precipitate was filtered and washed with ether several times to yield 0.50 g (65%) of **6a,** m.p.: 201°C; IR (cm^{-1}) (KBr): 3276 ν(br, NH and OH), 1719, 1645 ν(s, C=O), 1616–1475 (C···C, C···N, aromatic rings); ^1H NMR (d_6-DMSO, δ): 10.46 and 9.36 (br, OH and NH tautomers, respectively), 7.80–6.64 (m, 18H, Ar—H), 2.37 (s, 3H, CH_3), 2.12 ppm (s, 3H, CH_3); ^{13}C NMR (d_6-DMSO, δ): 191.14 (Ar—C=O), 181.71 (C-3), 164.21 (C-2), 148.79–122.41 (aromatic carbons), 115.34 (C-4), 92.21 (C-5), 23.08, 22.67 ppm (CH_3). Elemental analysis: found (calcd.): [C = 78.57 (78.46), H = 6.04 (5.52), N = 5.68 (5.90)].

3-Hydroxy-4-*p*-methylbenzoyl-1,5-di-*p*-tolyl-5-*p*-tolylamino-1,5-dihydro-2*H*-pyrrol-2-one (6b): To a solution of the compound **2** (0.30 g, 0.98 mmol) in benzene (40 mL) *p*-toluidine (0.21 g, 1.96 mmol) was added on an ice-bath. After the reaction mixture had been stirred at –5 to 0°C for 24 h the yellow-coloured precipitate was filtered and washed with ether to yield 0.39 g (80%) of **6b,** m.p.: 223°C; IR (cm^{-1}) (KBr): 3287 ν(br, NH and OH), 1716 ν(vs, C=O), 1620–1485 ν(C···C, C···N, aromatic rings); ^1H NMR (d_6-DMSO, δ): 10.75 (s, OH), 7.85–6.50 (m, 16H, Ar—H), 3.56 (br s, NH), 2.29 (s, 3H, CH_3), 2.22 (s, 3H, CH_3), 2.18 (s, 3H, CH_3), 2.14 ppm (s, 3H, CH_3); ^{13}C NMR (d_6-DMSO, δ): 190.08 (Ar—C=O), 181.90 (C-3), 164.00 (C-2), 147.27–121.55 (aromatic carbons), 116.15 (C-4), 90.98 (C-5), 22.99–21.03 ppm (4 × CH_3). Elemental analysis: found (calcd.): [C = 79.07 (78.86), H = 5.98 (6.02), N = 5.62 (5.57)].

3-Hydroxy-4-*p*-methylbenzoyl-5-*p*-tolyl-l-*o*-tolyl-5-*o*-tolylamino-1,5-dihydro-2*H*-pyrrol-2-one (6c): To a solution of the compound **2** (0.50 g, 1.63 mmol) in benzene (40 mL) *o*-toluidine (0.35 mL, 3.26 mmol) was added dropwise. After the reaction mixture had been stirred at room temperature for 2 days the

precipitate was filtered and washed with ether several times to yield 0.59 g (72%) of **6c**, m.p.: 217°C; IR (cm^{-1}) (KBr): 3280 ν(br, NH and OH), 1716, 1633 ν(s, C=O), 1617–1456 ν(C···C, C···N, aromatic rings); ^1H NMR (d_6-DMSO, δ): 7.90–6.48 (m, 16H, Ar—H), 2.37 (s, 3H, CH_3), 2.26 (s, 3H, CH_3), 2.19 (s, 3H, CH_3), 2.07 ppm (s, 3H, CH_3); ^{13}C NMR (d_6-DMSO, δ): 190.10 (Ar—C=O), 181.01 (C-3), 164.40 (C-2), 150.51–122.81 (aromatic carbons), 115.78 (C-4), 91.50 (C-5), 23.08, 22.89, 19.46, 19.22 ppm (CH_3). Elemental analysis: found (calcd.): [C = 78.79 (78.86), H = 6.14 (6.02), N = 5.48 (5.57)].

Synthesis of the 1*H*-Quinoxaline-2-ones (7): General Procedure

Apropriate amounts of 4-(4-methylbenzoyl)-5-(4-methylphenyl)furan-2,3-dione (**2**) and the corresponding 1,2-phenylenediamine derivative (molar ratio 1 : 1) were dissolved in benzene and stirred for 24 h at room temperature. The yellow-coloured precipitate was filtered off and recrystallized from the proper solvent (ethanol, *n*-butanol or *i*-propanol-DMF) and dried on P_2O_5.

3-(1,3-Dioxo-1,3-di-*p*-tolyl-2-propyl)-1*H*-quinoxalin-2-one (7a): This compound was obtained by the general procedure in 45% yield (0.29 g); m.p. 235°C (ethanol); IR (cm^{-1}) (KBr): 3448 ν(br, NH), 1694, 1660 ν(C=O), 1608, 1578, 1520, 1493; ^1H NMR (d_6-DMSO, δ): 12,63 (NH), 7.86–7.02 (m, 12H, Ar—H), 2.31 (s, 6H, CH_3); ^{13}C NMR (d_6-DMSO, δ); 195.28 (Ar—C=O), 161.02 (m, C_3=N), 156.33 (d, ^3J = 2 Hz, C-2), 147.85–117.43 (aromatic carbons), 60.89 (d, J_{CH} = 140 Hz, CH), 22.98, 22.81 ppm (CH_3). Elemental analysis: found (calcd.): [C = 75.86 (75.74), H = 4.98 (5.08), N = 7.16 (7.07)].

3-(1,3-Dioxo-1,3-di-*p*-tolyl-2-propyl)-7-methyl-1*H*-quinoxalin-2-one (7b): This compound was obtained by the general procedure in 51% yield (0.34 g); m.p. 258°C (*n*-propanol); IR (cm^{-1}) (KBr): 3465 ν(br, NH), 1695, 1661 ν(C=O), 1605, 1575, 1563, 1518, 1498; ^1H NMR (d_6-DMSO, δ): 12,60 (NH), 7.91–7.06 (m, 11H, Ar—H), 2.39 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 2.33 ppm (s, 3H, CH_3); ^{13}C NMR (d_6-DMSO, δ): 195.39 (Ar—C=O), 160.01 (m, C_3 = N), 158.06 (d, ^3J = 2.2 Hz, C-2), 155.87–116.91 (aromatic carbons), 60.85 (d, J_{CH} = 142 Hz, CH), 22.96, 21.97 ppm (CH_3). Elemental analysis: found (calcd.): [C = 76.16 (76.08), H = 5.54 (5.40), N = 6.92 (6.82)].

3-(1,3-Dioxo-1,3-di-*p*-tolyl-2-propyl)-6,7-dimethyl-1*H*-quinoxalin-2-one (7c): This compound was obtained by the general procedure in 48% yield (0.33 g); m.p. 301°C (*n*-butanol); IR (cm^{-1}) (KBr): 3443 ν(br, NH), 1694, 1659 ν(C=O), 1605, 1575, 1497; ^1H NMR (d_6-DMSO, δ): 12.55 (NH), 7.91–6.95 (m, 10H, Ar—H), 2.37 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 2.21 (s, 3H, CH_3); ^{13}C NMR (d_6-DMSO, δ): 195.43 (Ar—C=O), 157.96 (m, C_3 = N), 155.61 (d, ^3J = 2 Hz, C-2), 145.91–117.28 (aromatic carbons), 60.78 (d, J_{CH} = 139 Hz, CH), 22.95, 21.53, 20.46 ppm (CH_3). Elemental analysis: found (calcd.): [C = 76.25 (76.39), H = 5.61 (5.70), N = 6.53 (6.60)].

3-(1,3-Dioxo-1,3-di-*p*-tolyl-2-propyl)-6-nitro-1*H*-quinoxalin-2-one (7d):

This compound was obtained by the general procedure in 68% yield (0.49 g); m.p. 317°C (2-propanol-DMF); IR (cm^{-1}) (KBr): 3445–3200 ν(br, NH), 1698, 1680, 1656 ν(C=O), 1591, 1573, 1534 ν(C···C, C···N or N···O), 1332 (s, N···O); ^1H NMR (d_6-DMSO, δ): 8.20–7.33 (m, 11H, Ar—H), 7.16 (br, NH), 2.38 (s, 3H, CH_3) 2.30 ppm (br, s, 3H, CH_3); ^{13}C NMR (d_6-DMSO, δ): 194.81 (Ar—C=O), 161.30 (m, C_3=N), 157.56 (d, $^3J = 2.3$ Hz, C-2), 155.24–117.85 (aromatic carbons), 61.34 (d, $J_{CH} = 143$ Hz, CH), 22.96, 22.79 ppm (CH_3). Elemental analysis: found (calcd.): [C = 68.19 (68.02), H = 4.32 (4.34), N = 9.68 (9.52)].

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