

Five-Membered 2,3-Dioxoheterocycles: LXXXIV.* [4+2]-Cycloaddition of Styrene to 4,5-Diaroyl-1*H*-pyrrole-2,3-diones. Crystal and Molecular Structures of 7a-(2,5-Dimethylbenzoyl)-4-(2,5-dimethylphenyl)-1-(4-methoxyphenyl)-6-phenyl-7,7a-dihydropyrano[4,3-*b*]-pyrrole-2,3(1*H*,6*H*)-dione

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Abstract—1-Aryl-4,5-diaroyl-1*H*-pyrrole-2,3-diones react with styrene to form substituted 7,7a-dihydropyrano[4,3-*b*]pyrrole-2,3(1*H*,6*H*)-diones whose structure was confirmed by XRD analysis. The crystal and molecular structure of 7a-(2,5-dimethylbenzoyl)-4-(2,5-dimethylphenyl)-1-(4-methoxyphenyl)-6-phenyl-7,7a-dihydropyrano[4,3-*b*]pyrrole-2,3(1*H*,6*H*)dione was examined.

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1*H*-Pyrrole-2,3-diones exhibited a considerable reactivity in the Diels–Alder reactions [2, 3]. Polar olefins took part in the [4+2]-cycloaddition at the conjugated bonds system C⁵=C⁴–C=O of the 4-benzoyl-1-phenyl-5-ethoxycarbonyl-1*H*-pyrrole-2,3-dione that was applied to the building up of the heterocyclic system of pyrano[4,3-*b*]pyrrole [4, 5]. The olefins cycloaddition to 4,5-diaroyl-1*H*-pyrrole-2,3-diones was not formerly investigated.

With the goal to investigate the influence of the introduction of an aroyl fragment into the position 5 of the 1*H*-pyrrole-2,3-diones on the direction of the cycloaddition we studied the reactions of 1-aryl-4,5-diaroyl-1*H*-pyrrole-2,3-diones **Ia–Ig** with styrene. Pyrrolediones **Ia–Id** [1] were prepared by known procedures, and pyrrolediones **If, Ig** were obtained for the first time by the reaction of (*Z*)-1,4-diaryl-2-arylamino-but-2-ene-1,4-diones **IIa, IIb** with oxalyl chloride. Compounds **IIa, IIb** were obtained in their turn by the reaction of diacylacetylenes **IIIa, IIIb** [6, 7] with *p*-toluidine.

The boiling of pyrrolediones **Ia–Ig** and styrene in

the ratio 1:1.5 in *m*-xylene solution over 5–8 h (TLC monitoring) afforded 1,4-diaryl-7a-aroyl-6-phenyl-7,7a-dihydropyrano[4,3-*b*]pyrrole-2,3(1*H*,6*H*)-diones **IVa–IVg** whose structure was proved by XRD analysis by an example of compound **IVe**.

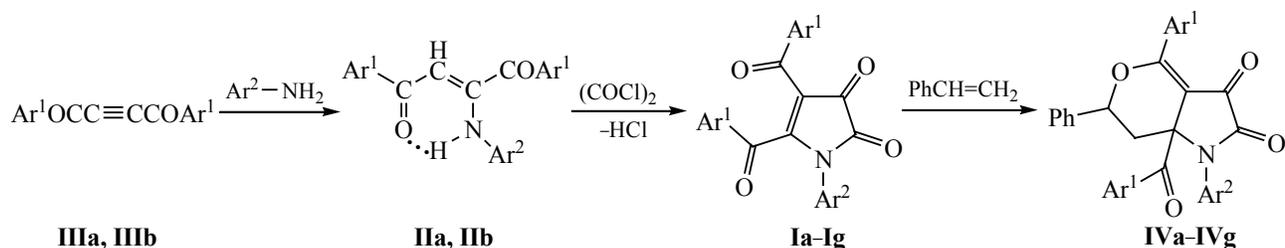
Compounds **IVa–IVg** are light-yellow or colorless crystalline substances of high melting points, readily soluble in the common organic solvents, insoluble in alkanes and water.

The IR spectra of compounds **IVa–IVg** contain the absorption bands of the stretching vibrations of lactam C²=O and ketone C³=O carbonyl groups as one broad or two narrow bands at 1698–1725 cm^{−1}, and of the aroyl carbonyl group in the region 1684–1688 cm^{−1}.

In the ¹H NMR spectra of compounds **IVa–IVg** alongside the signals of the protons of the aromatic rings and of the groups connected thereto multiplets are present of the methine proton (5.36–5.67 ppm) and of the protons of the methylene group in the region 2.63–2.98 ppm forming a typical *ABX* system.

The ¹³C NMR spectra of compounds **IVa, IVg** alongside the signals of the carbon atoms of the aromatic rings

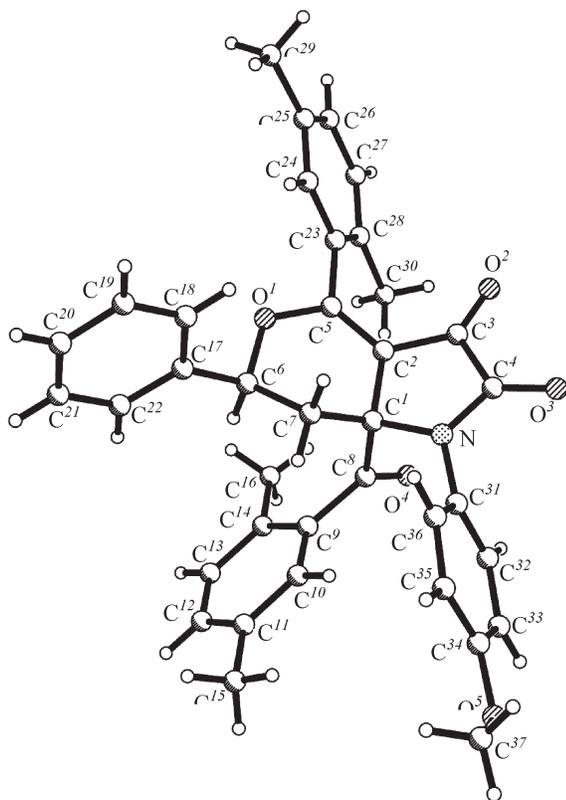
* For Communication LXXXIII, see [1].



I, IV, Ar¹ = Ar² = Ph (**a**); Ar¹ = C₆H₃Me₂-2,5, Ar² = Ph (**b**); Ar¹ = Ph, Ar² = C₆H₄OMe-4 (**c**); Ar¹ = C₆H₄Me-4, Ar² = Ph (**d**); Ar¹ = C₆H₃Me₂-2,5, Ar² = C₆H₄OMe-4 (**e**); Ar¹ = Ph, Ar² = C₆H₄Me-4 (**f**); Ar¹ = Ar² = C₆H₄Me-4 (**g**); **II, III**, Ar¹ = Ph, Ar² = C₆H₄Me-4 (**a**); Ar¹ = Ar² = C₆H₄Me-4 (**b**).

and of the groups connected thereto contain the carbon signals of the aroyl carbonyl group (197.52–198.60 ppm), keto and lactame carbonyls of the pyrroledione ring (177.64–177.67 and 162.05–162.17 ppm respectively), and also the signals of the carbon atoms in the positions 6, 7, and 7a of the pyrano[4,3-*b*]pyrrole-2,3-dione ring (79.48–79.51, 34.62–35.09, and 66.05–66.10 ppm respectively).

The spectra characteristics of compounds and of the



General view of the molecule of 7a-(2,5-dimethylbenzoyl)-4-(2,5-dimethylphenyl)-1-(4-methoxyphenyl)-6-phenyl-7,7a-dihydroprano[4,3-*b*]pyrrole-2,3(1*H*,6*H*)-dione (**IVe**).

groups connected thereto are very similar to those of previously described (3*R**, 4*aR**)-4,4a,6,7-tetrahydro-6,7-dioxo-1,3,5-triphenyl-4a-ethoxycarbonyl-5*H*-pyrano[4,3-*b*]pyrrole [4].

By the XRD data (see the figure) the pyran ring of the molecule of compound **IVe** exists in the envelop conformation. The bend at the line C¹...C⁶ is 49.6°, and the deviation of the C⁷ atom from the plane of the rest five atoms is 0.67 Å. All bonds and angles in the molecule have the values common for the corresponding atoms. The bond C²=C⁵ is a localized double bond, 1.354(5) Å. The pyrrole ring is planar within 0.01 Å and forms with the plane of five pyran atoms a dihedral angle of 153.4°. No hydrogen bonds and shortened contacts were found in the crystal. The formation of compounds **IVa–IVg** occurs evidently due to the involvement of the conjugated bond system O=C–C⁴=C⁵ of pyrrolediones **Ia–Ig** in the thermally induced reaction of the [4+2]-cycloaddition to the polarized C=C bond of styrene.

EXPERIMENTAL

IR spectra of compounds obtained were recorded on a spectrophotometer FSM-1201 from mulls in mineral oil. ¹H and ¹³C NMR spectra were registered on a spectrometer Bruker AM-400 [operating frequencies 400 (¹H) and 100 (¹³C) MHz] in DMSO-*d*₆, internal reference TMS. The homogeneity of compounds obtained was confirmed by TLC on Silufol plates, eluents benzene–ethyl acetate, 5:1, ethyl acetate, development in iodine vapor or under UV irradiation.

4,5-Dibenzoyl-1-(4-tolyl)-1*H*-pyrrole-2,3-dione (If). To 0.01 mol of compound **IIa** in 50 ml of anhydrous benzene was added dropwise a solution of 0.011 mol of freshly distilled oxalyl chloride in 10 ml of anhydrous benzene, the mixture was boiled for 80 min, cooled,

the separated precipitate was filtered off. Yield 67%, mp 215–216°C (decomp., benzene). IR spectrum, cm^{-1} : 1769 ($\text{C}^2=\text{O}$), 1727 ($\text{C}^3=\text{O}$), 1671 ($\text{C}^4-\text{C}=\text{O}$), 1649 ($\text{C}^5-\text{C}=\text{O}$). ^1H NMR spectrum, δ , ppm: 2.26 s (3H, Me), 7.15–8.14 group of signals (14H, 2Ph + C_6H_4). Found, %: C 75.92; H 4.37; N 3.55. $\text{C}_{25}\text{H}_{17}\text{NO}_4$. Calculated, %: C 75.94; H 4.33; N 3.54.

4,5-Di(4-toluoyl)-1-(4-tolyl)-1H-pyrrole-2,3-dione (Ig) was similarly synthesized. Yield 65%, mp 222–223°C (decomp., benzene). IR spectrum, cm^{-1} : 1775 ($\text{C}^2=\text{O}$), 1725 ($\text{C}^3=\text{O}$), 1672 ($\text{C}^4-\text{C}=\text{O}$), 1645 ($\text{C}^5-\text{C}=\text{O}$). ^1H NMR spectrum, δ , ppm: 2.24 s (3H, Me), 2.33 s (3H, Me), 2.38 s (3H, Me), 7.14–8.04 group of signals (12H, $3\text{C}_6\text{H}_4$). Found, %: C 76.54; H 5.03; N 3.33. $\text{C}_{27}\text{H}_{21}\text{NO}_5$. Calculated, %: C 76.58; H 5.00; N 3.31.

(Z)-2-(4-Tolylamino)-1,4-diphenylbut-2-ene-1,4-dione (IIa). A solution of 0.01 mol of dibenzoylacetylene (IIIa) [6] and 0.01 mol of *p*-toluidine in 30 ml of anhydrous benzene was boiled for 5 min (TLC monitoring), 30 ml of warm petroleum ether (40–70) was added, the mixture was cooled, the separated precipitate was filtered off. Yield 91%, mp 153–154°C (benzene–petroleum ether, 1 : 1). IR spectrum, cm^{-1} : 3150 br. (NH), 1678 ($\text{C}^1=\text{O}$), 1600 br. ($\text{C}^4=\text{O}$ in intramolecular hydrogen bond). ^1H NMR spectrum, δ , ppm: 2.33 s (3H, Me), 6.56 s (1H, CH), 6.92–8.03 group of signals (14H, 2Ph + C_6H_4), 12.43 br. C (1H, NH). Found, %: C 80.94; H 5.58; N 4.13. $\text{C}_{23}\text{H}_{19}\text{NO}_2$. Calculated, %: C 80.92; H 5.61; N 4.10.

(Z)-1,4-Di(4-tolyl)-2-(4-tolylamino)but-2-ene-1,4-dione (IIb) was similarly synthesized. Yield 89%, mp 169–170°C (benzene–petroleum ether, 1 : 1). IR spectrum, cm^{-1} : 3160 br. (NH), 1665 ($\text{C}^1=\text{O}$), 1605 br. ($\text{C}^4=\text{O}$ c CCC). ^1H NMR spectrum, δ , ppm: 2.17 s (3H, Me), 2.36 s (6H, 2Me), 6.13 s (1H, CH), 6.91–7.87 group of signals (12H, $3\text{C}_6\text{H}_4$), 12.43 br. s (1H, NH). Found, %: C 81.25; H 6.30; N 3.75. $\text{C}_{25}\text{H}_{23}\text{NO}_2$. Calculated, %: C 81.27; H 6.27; N 3.79.

7a-Benzoyl-1,4,6-triphenyl-7,7a-dihydropyrano[4,3-*b*]pyrrole-2,3(1H,6H)-dione (IVa). To a solution of 1.0 mmol of compound Ia in 25 ml of anhydrous *m*-xylene was added a solution of 1.5 mmol of styrene in 10 ml of anhydrous *m*-xylene, the mixture was boiled for 8 h, cooled, the separated precipitate was filtered off. Yield 87%, mp 232–233°C (toluene). IR spectrum, cm^{-1} : 1723 ($\text{C}^2=\text{O}$), 1698 ($\text{C}^3=\text{O}$), 1678 ($\text{C}^7\text{a}-\text{C}=\text{O}$). ^1H NMR spectrum, δ , ppm: 2.69 t (1H, CH_2 , J 12.4 Hz), 2.98 d.d (1H, CH_2 , J 12.4, J 3.6 Hz), 5.67 d.d (1H, CH, J 12.4, J 3.6 Hz), 7.16–7.76 group of signals (20H, 4Ph).

^{13}C NMR spectrum, δ , ppm: 34.62 (C^7), 66.05 (C^7a), 79.48 (C^6), 104.60 (C^3a), 126.43–138.50 (C_{arom}), 162.05 (C^2), 166.23 (C^4), 177.64 (C^3), 198.60 ($\text{C}^7\text{a}-\text{CO}$). Found, %: C 79.13; H 4.74; N 2.84. $\text{C}_{32}\text{H}_{23}\text{NO}_4$. Calculated, %: C 79.16; H 4.77; N 2.88.

Compounds IVb–IVg were prepared in analogous way.

7a-(2,5-Dimethylbenzoyl)-4-(2,5-dimethylphenyl)-1,6-diphenyl-7,7a-dihydropyrano[4,3-*b*]pyrrole-2,3(1H,6H)-dione (IVb). Yield 73%, mp 254–255°C (ethyl acetate–acetone–benzene, 1 : 1 : 1). IR spectrum, cm^{-1} : 1725 ($\text{C}^2=\text{O}$, $\text{C}^3=\text{O}$), 1686 ($\text{C}^7\text{a}-\text{C}=\text{O}$). ^1H NMR spectrum, δ , ppm: 2.08 s (3H, Me), 2.12 s (3H, Me), 2.17 s (3H, Me), 2.28 s (3H, Me), 2.72 t (1H, CH_2 , J 12.8 Hz), 2.95 d.d (1H, CH_2 , J 12.8, J 3.2 Hz), 5.41 d.d (1H, CH, J 12.8, J 3.2 Hz), 6.93–7.54 group of signals (16H, 2Ph + $2\text{C}_6\text{H}_3$). Found, %: C 79.77; H 5.71; N 2.55. $\text{C}_{36}\text{H}_{31}\text{NO}_4$. Calculated, %: C 79.83; H 5.77; N 2.59.

7a-Benzoyl-1-(4-methoxyphenyl)-4,6-diphenyl-7,7a-dihydropyrano[4,3-*b*]pyrrole-2,3(1H,6H)-dione (IVc). Yield 78%, mp 239–240°C (toluene–ethyl acetate–acetone, 1 : 1 : 1). IR spectrum, cm^{-1} : 1717 ($\text{C}^2=\text{O}$), 1700 ($\text{C}^3=\text{O}$), 1688 ($\text{C}^7\text{a}-\text{C}=\text{O}$). ^1H NMR spectrum, δ , ppm: 2.67 t (1H, CH_2 , J 12.4 Hz), 2.95 d.d (1H, CH_2 , J 12.4, J 3.6 Hz), 3.76 s (3H, OMe), 5.62 d.d (1H, CH, J 12.4, J 3.6 Hz), 6.99–7.75 group of signals (19H, 3Ph + C_6H_4). Found, %: C 76.85; H 4.86; N 2.68. $\text{C}_{33}\text{H}_{25}\text{NO}_5$. Calculated, %: C 76.88; H 4.89; N 2.72.

4-(4-Tolyl)-7a-(4-toluoyl)-1,6-diphenyl-7,7a-dihydropyrano[4,3-*b*]pyrrole-2,3(1H,6H)-dione (IVd). Yield 84%, mp 249–250°C (ethyl acetate). IR spectrum, cm^{-1} : 1719 ($\text{C}^2=\text{O}$), 1700 ($\text{C}^3=\text{O}$), 1684 ($\text{C}^7\text{a}-\text{C}=\text{O}$). ^1H NMR spectrum, δ , ppm: 2.40 s (6H, 2Me), 2.65 t (1H, CH_2 , J 12.4 Hz), 2.96 d.d (1H, CH_2 , J 12.4, J 3.6 Hz), 5.64 d.d (1H, CH, J 12.4, J 3.6 Hz), 7.10–7.66 group of signals (18H, 2Ph + $2\text{C}_6\text{H}_4$). Found, %: C 79.43; H 5.25; N 2.65. $\text{C}_{34}\text{H}_{27}\text{NO}_4$. Calculated, %: C 79.51; H 5.30; N 2.73.

7a-(2,5-Dimethylbenzoyl)-4-(2,5-dimethylphenyl)-1-(4-methoxyphenyl)-6-phenyl-7,7a-dihydropyrano[4,3-*b*]pyrrole-2,3(1H,6H)-dione (IVe). Yield 76%, mp 264–265°C (toluene). IR spectrum, cm^{-1} : 1723 ($\text{C}^2=\text{O}$, $\text{C}^3=\text{O}$), 1688 ($\text{C}^7\text{a}-\text{C}=\text{O}$). ^1H NMR spectrum, δ , ppm: 2.06 s (3H, Me), 2.13 s (3H, Me), 2.18 s (3H, Me), 2.27 s (3H, Me), 2.71 t (1H, CH_2 , J 12.8 Hz), 2.90 d.d (1H, CH_2 , J 12.8, J 3.2 Hz), 3.78 s (3H, OMe), 5.36 d.d (1H,

CH, J 12.8, J 3.2 Hz), 6.93–7.50 group of signals (15H, Ph + C₆H₄ + 2C₆H₃). Found, %: C 77.69; H 5.79; N 2.40. C₃₇H₃₃NO₅. Calculated, %: C 77.74; H 5.82; N 2.45.

XRD analysis of compound IVe. Colorless bulky crystals of C₃₇H₃₃NO₅ belong to the monoclinic crystal system: a 13.803(3), b 11.607(2), c 18.969(4) Å, β 91.88(3)°, V 3037.4(11) Å³, M 571.64, d_{calc} 1.250 g cm⁻³, Z 4, space group $P21/C$. The set of experimental reflections was obtained on an automatic four-circle diffractometer QM-4 (KUMA DIFFRACTION) with the χ -geometry by the method of $\omega/2\theta$ scanning in the monochromatized MoK α -radiation ($2\theta \leq 50^\circ$). Overall 6057 reflections were measured, among them 4775 independent (R_{int} 0.0714). No correction for extinction was introduced (μ 0.083 mm⁻¹). The structure was solved by the direct method with the use of SIR92 software [8] followed by the series of electron density maps calculations. Hydrogen atoms were placed geometrically. Full-matrix anisotropic (for nonhydrogen atoms) least-squares refinement along the software SHELXL-97 [9] was ended at R_1 0.0726 for 2044 reflections with $I \geq 2\sigma(I)$ and R_1 0.1913 for all reflections. Refined parameters 389, $\Delta\rho_{\text{max}}$ 0.218 Å⁻³. $GOOF$ 0.955. The crystallographic data are deposited in the Cambridge Crystallographic Data Center (CCDC no. 827017).

7a-Benzoyl-1-(4-tolyl)-4,6-diphenyl-7,7a-dihydropyrano[4,3-*b*]pyrrole-2,3(1*H*,6*H*)-dione (IVf). Yield 79%, mp 243–244°C (*O*-xylene). IR spectrum, cm⁻¹: 1721 (C²=O), 1701 (C³=O), 1688 (C^{7a}-C=O). ¹H NMR spectrum, δ , ppm: 2.31 s (3H, Me), 2.66 t (1H, CH₂, J 12.2 Hz), 2.97 d.d (1H, CH₂, J 12.2, J 3.5 Hz), 5.64 d.d (1H, CH, J 12.2, J 3.5 Hz), 7.02–7.74 group of signals (19H, 3Ph + C₆H₄). Found, %: C 79.30; H 5.00; N 2.77. C₃₃H₂₅NO₄. Calculated, %: C 79.34; H 5.04; N 2.80.

1,4-Di(4-tolyl)-7a-(4-toluoyl)-6-phenyl-7,7a-dihydropyrano[4,3-*b*]pyrrole-2,3(1*H*,6*H*)-dione (IVg). Yield 82%, mp 212–213°C (toluene). IR spectrum, cm⁻¹: 1725 (C²=O), 1705 (C³=O), 1685 (C^{7a}-C=O). ¹H, δ , ppm: 2.30 s (3H, Me), 2.40 s (6H, 2Me), 2.63 t (1H, CH₂, J 12.8 Hz), 2.96 d.d (1H, CH₂, J 12.8, J 3.6 Hz), 5.62 d.d (1H, CH, J 12.8, J 3.6 Hz), 6.98–7.67 group of signals (17H, Ph + 3C₆H₄). ¹³C NMR spectrum, δ , ppm: 20.50 (Me), 20.97 (Me), 21.20 (Me), 35.09 (C⁷), 66.10 (C^{7a}), 79.51 (C⁶), 104.48 (C^{3a}), 126.44–143.10 (C_{arom}), 162.17 (C²), 166.26 (C⁴), 177.67 (C³), 197.52 (C^{7a}-C=O). Found, %: C 79.59; H 5.50; N 2.62. C₃₅H₂₉NO₄. Calculated, %: C 79.68; H 5.54; N 2.65.

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