

SHORT COMMUNICATIONS

New Pathway of the Reaction of Hetareno[*a*]pyrrole-2,3-diones with NH Nucleophiles

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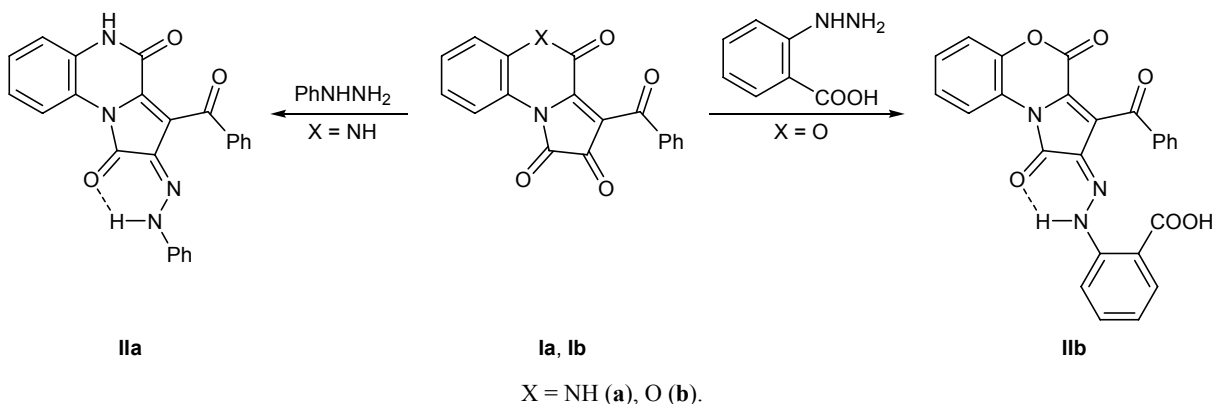
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It was shown previously that 4-acyl-1*H*-pyrrole-2,3-diones fused at the N¹–C⁵ bond to various heterocycles (hetareno[*a*]pyrrole-2,3-diones) react with mono- and difunctional nucleophiles via initial addition at the C¹ or C^{3a} carbon atom of the hetareno[*a*]pyrrole skeleton [1].

By reactions of 3-benzoylpyrrolo[1,2-*a*]quinoxaline-1,2,4(5*H*)-trione (**Ia**) with phenylhydrazine and of 3-benzoyl-1*H*-benzo[*b*]pyrrolo[1,2-*d*][1,4]oxazine-1,2,4-trione (**Ib**) with 2-hydrazinobenzoic acid (reactant molar ratio 1:1, anhydrous acetonitrile, 1–3 min under reflux; TLC monitoring), we obtained products resulting from nucleophilic attack at the C² carbon atom, (Z)-3-benzoyl-2-(2-phenylhydrazono)pyrrolo[1,2-*a*]quinoxaline-1,4(2*H*,5*H*)-dione (**IIa**) and (Z)-2-{2-(3-benzoyl)-1,4-dioxo-1*H*-benzo[*b*]pyrrolo[1,2-*d*][1,4]-oxazin-2(4*H*)-ylidenehydrazino}benzoic acid (**IIb**). The product structure was proved by X-ray analysis of compound **IIb**.

Although the possibility for other (than those indicated above [1]) direction of nucleophilic attack on 4-acyl-1*H*-pyrrole-2,3-diones fused at the N¹–C⁵ bond to various heterocycles was theoretically predicted about 20 years ago [2], products of such reactions were isolated for the first time.

(Z)-3-Benzoyl-2-(2-phenylhydrazono)pyrrolo[1,2-*a*]quinoxaline-1,4(2*H*,5*H*)-dione (IIa). A solution of 1.0 mmol of phenylhydrazine in 10 ml of anhydrous acetonitrile was added to a solution of 1.0 mmol of compound **Ia** in 30 ml of anhydrous acetonitrile. The mixture was heated for 3 min under reflux and cooled, and the precipitate was filtered off. Yield 69%, mp 241–243°C (from DMF). IR spectrum, ν , cm^{–1}: 3350, 3200 (NH); 1680 (C¹=O); 1660 (C⁴=O); 1630 (COPh). ¹H NMR spectrum, δ , ppm: 6.99–7.68 m (11H, H_{arom}), 8.03 d (2H, *o*-H in COPh, *J* = 7.4 Hz), 8.69 d (1H, 9-H, *J* = 7.4 Hz), 11.22 s (1H, 5-H), 13.31 s (1H, NHPh). Found, %: C 70.53; H 3.91;



N 13.75. $C_{24}H_{16}N_4O_3$. Calculated, %: C 70.58; H 3.95; N 13.72.

2-[(Z)-2-(3-Benzoyl-1,4-dioxo-1H-benzo[b]pyrrolo[1,2-d][1,4]oxazin-2(4H)-ylidene)hydrazino]-benzoic acid (IIb). A solution of 1.0 mmol of 2-hydrazinobenzoic acid hydrochloride in 30 ml of a 10:1 mixture of anhydrous acetonitrile and DMSO was added to a solution of 1.0 mmol of compound **Ib** in 30 ml of anhydrous acetonitrile. The mixture was heated for 1 min under reflux and cooled, and the precipitate was filtered off. Yield 47%, mp 275–277°C (from acetonitrile). IR spectrum, ν , cm^{-1} : 3300 br, 3200 (OH, NH), 1732 ($C^1=O$), 1669 (COOH), 1636 (COPh). 1H NMR spectrum, δ , ppm: 7.23–8.12 m (12H, H_{arom}), 8.63 d (1H, 9-H, $J = 8.0$ Hz), 10.24 s (1H, 5-H), 13.70 s (1H, COOH), 14.87 s (1H, NH). Found, %: C 66.21; H 3.29; N 9.24. $C_{25}H_{15}N_3O_6$. Calculated, %: C 66.23; H 3.33; N 9.27.

The X-ray diffraction data for compound **IIb** were acquired on an Xcalibur S automatic diffractometer [$\lambda(MoK_{\alpha})$ 0.71073 Å, temperature 295(2) K, ω -scanning through a step of 1°, crystal to detector distance 50 mm] according to standard procedure. Total of 7184 reflections were measured, 5783 of which were

independent (R_{int} 0.0304) and 2438 reflections were characterized by $I > 2\sigma(I)$. No correction for absorption was introduced. Triclinic crystal, space group $P-1$; unit cell parameters: $a = 8.463(2)$, $b = 11.609(3)$, $c = 12.8717(19)$ Å; $\alpha = 83.952(16)$, $\beta = 76.505(17)$, $\gamma = 85.75(2)^\circ$. Final divergence factors: $R_1 = 0.0394$, $wR_2 = 0.0775$ for reflections with $I > 2\sigma(I)$; goodness of fit $S = 1.004$; maximal and minimal residual electron densities 0.347 and -0.185 $\bar{e}/\text{\AA}^3$.

The IR spectra were recorded on an FSM-1201 spectrometer from samples dispersed in mineral oil. The 1H NMR spectra were obtained on a Bruker AM-400 instrument (400 MHz) using DMSO- d_6 as solvent and tetramethylsilane as internal reference.

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