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Five-Membered 2,3-Dioxo Heterocycles: XCVII.* Reaction of 3-Aroylpyrrolo[1,2-*a*]quinoxaline-1,2,4(5*H*)-triones with Fischer's Base

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Abstract—3-Aroylpyrrolo[1,2-*a*]quinoxaline-1,2,4(5*H*)-triones reacted with 1,3,3-trimethyl-2-methylidene-2,3-dihydro-1*H*-indole (Fischer's base) to give (2*Z*)-1-aryl-2-[3-oxo-3,4-dihydroquinoxalin-2(1*H*)-ylidene]-5-(1,3,3-trimethyl-2,3-dihydro-1*H*-indol-2-ylidene)pentane-1,3,4-triones.

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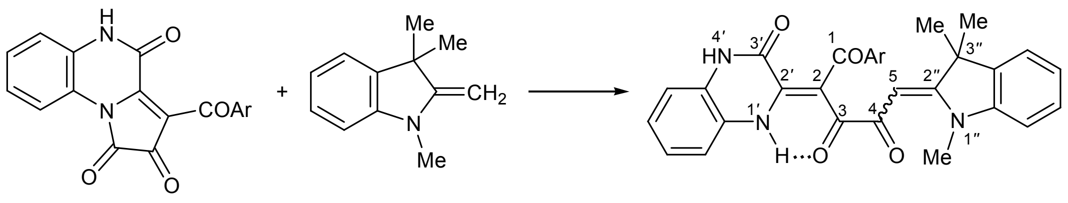
Substituted 4-acyl-1*H*-pyrrole-2,3-diones, including those fused by the [*e*] side to aza heterocycles, readily react with binucleophiles to produce a variety of fused heterocyclic and spiro-heterocyclic systems [2–4]. We previously studied reactions of 4-acyl-1*H*-pyrrole-2,3-diones fused to quinoxalin-2-one fragment, 3-aroylpyrrolo[1,2-*a*]quinoxaline-1,2,4(5*H*)-triones, with primary enamines. The reactions of pyrroloquinoxalinetriones with *N*-alkyl-substituted dimedone imines involved successive addition of the β-CH and NH groups in the enamine fragment of the latter (enamine tautomer) to the C^{3a} and C^2 atoms of pyrroloquinoxalinetrione, respectively, to give bridged 3,10,13-triazapentacyclo-$[10.7.1.0^{1,10}.0^{4,9}.0^{14,19}]$icosanes [4, 5]. The reaction of pyrroloquinoxalinetriones with substituted 1,3,3-trimethyl-2-azaspiro[4.5]dec-1-enes stops at the stage of addition of the β-CH group of the enamine to the C^{3a} atom of pyrroloquinoxalinetrione [1]. Reactions of 3-aroylpyrrolo[1,2-*a*]quinoxaline-1,2,4(5*H*)-triones with secondary enamines were not reported.

By heating 3-aroylpyrrolo[1,2-*a*]quinoxaline-1,2,4(5*H*)-triones **Ia**–**Ie** with an equimolar amount of 1,3,3-trimethyl-2-methylidene-2,3-dihydro-1*H*-indole (**II**, Fischer's base) in boiling anhydrous acetonitrile for 2–10 min (until disappearance of bright violet color typical of initial pyrroloquinoxalinetriones) we obtained in good yields the corresponding (2*Z*)-1-aryl-2-[3-oxo-3,4-dihydroquinoxalin-2(1*H*)-ylidene]-5-(1,3,3-trimethyl-2,3-dihydro-1*H*-indol-2-ylidene)pentane-1,3,4-triones **IIIa**–**IIIe** (Scheme 1).

Compounds **IIIa**–**IIIe** were isolated as orange or red high-melting (with decomposition) crystalline substances, which were readily soluble in DMSO and DMF, poorly soluble in alcohols and chlorinated hydrocarbons, and insoluble in water and alkanes. The IR spectra of **IIIa**–**IIIe** contained absorption bands due to stretching vibrations of NH group (3175–3185 cm^{-1}), NH group involved in intramolecular hydrogen bond (broadened band, 3093–3098 cm^{-1}), and carbonyl groups ($C^{3'}$=O, C^4=O, 1678–1688 cm^{-1};

Scheme 1.



Ia–Ie **II** **IIIa–IIIe**

Ar = Ph (**a**), 4-MeC_6H_4 (**b**), 4-$MeOC_6H_4$ (**c**), 4-ClC_6H_4 (**d**), 4-BrC_6H_4 (**e**).

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* For communication XCVI, see [1].

ArC=O, 1651–1653 cm^{-1}; C^3=O, 1605–1609 cm^{-1}, broadened band). In the ^{1}H NMR spectra of **IIIa–IIIe** we observed signals from aromatic protons, a six-proton singlet at δ 1.43–1.48 ppm from two methyl groups in position *3* of the indole fragment, a three-proton singlet at δ 3.27–3.29 ppm from the NCH$_3$ group, a singlet at δ 5.81–5.83 ppm from the vinylic proton, a singlet at δ 12.04–12.05 ppm from the NH proton in position *4* of the quinoxaline ring, and a singlet at δ 14.46–14.52 ppm from the NH proton (H-bonded) in position *1* of the quinoxaline fragment.

Presumably, in the described reaction attack by the =CH$_2$ group of Fischer's base on the C^1 atom of **Ia**–**Ie** is followed by opening of the pyrrole ring via cleavage of the C^1–N^{10} bond, as described in [2–4] for the reactions of 3-aroylpyrrolo[1,2-*a*]quinoxaline-1,2,4(5*H*)-triones with mononucleophiles. No such pathway was observed previously in reactions of pyrroloquinoxalinetriones with enamines.

EXPERIMENTAL

The IR spectra were recorded on a Bruker IFS 66 spectrometer with Fourier transform from samples dispersed in mineral oil. The ^{1}H and ^{13}C NMR spectra were measured on a Varian Mercury-300BB spectrometer (300 MHz for ^{1}H) from solutions in DMSO-d_6 using hexamethyldisiloxane as internal reference. The purity of the isolated compounds was checked by TLC on Sorbfil plates using ethyl acetate–benzene (1:5) or ethyl acetate as eluent; spots were visualized by treatment with iodine vapor.

(2*Z*)-2-[3-Oxo-3,4-dihydroquinoxalin-2(1*H*)-ylidene]-1-phenyl-5-(1,3,3-trimethyl-2,3-dihydro-1*H*-indol-2-ylidene)pentane-1,3,4-trione (IIIa). A solution of 1.0 mmol of compound **Ia** and 1.0 mmol of Fischer's base (**II**) in 20 mL of anhydrous acetonitrile was heated for 10 min and cooled, and the precipitate was filtered off. Yield 89%, mp 177–179°C (from dichloroethane). IR spectrum, ν, cm^{-1}: 3185 (NH), 3095 br (NH, H-bonded), 1680 (C$^{3'}$=O, C^4=O), 1653 (C^1=O), 1608 (C^3=O, H-bonded). ^{1}H NMR spectrum, δ, ppm: 1.47 s (6H, Me), 3.29 s (3H, NMe), 5.83 s (1H, CH), 7.03–8.02 m (13H, H$_{\text{arom}}$), 12.05 s (1H, N$^{4'}$H), 14.52 s (1H, N$^{1'}$H). Found, %: C 73.12; H 5.25; N 8.52. C$_{30}$H$_{25}$N$_3$O$_4$. Calculated, %: C 73.30; H 5.13; N 8.55.

Compounds **IIIb–IIIe** were synthesized in a similar way.

(2*Z*)-1-(4-Methylphenyl)-2-[3-oxo-3,4-dihydroquinoxalin-2(1*H*)-ylidene]-5-(1,3,3-trimethyl-2,3-dihydro-1*H*-indol-2-ylidene)pentane-1,3,4-trione (IIIb). Yield 90%, mp 169–171°C (from EtOAc). IR spectrum, ν, cm^{-1}: 3175 (NH), 3094 br (NH, H-bonded), 1678 (C$^{3'}$=O, C^4=O), 1653 (C^1=O), 1605 (C^3=O, H-bonded). ^{1}H NMR spectrum, δ, ppm: 1.48 s (6H, Me), 2.35 s (3H, 4-**Me**C$_6$H$_4$), 3.28 s (3H, NMe), 5.81 s (1H, CH), 7.02–7.94 m (12H, H$_{\text{arom}}$), 12.04 s (1H, N$^{4'}$H), 14.50 s (1H, N$^{1'}$H). Found, %: C 73.59; H 5.51; N 8.21. C$_{31}$H$_{27}$N$_3$O$_4$. Calculated, %: C 73.65; H 5.38; N 8.31.

(2*Z*)-1-(4-Methoxyphenyl)-2-[3-oxo-3,4-dihydroquinoxalin-2(1*H*)-ylidene]-5-(1,3,3-trimethyl-2,3-dihydro-1*H*-indol-2-ylidene)pentane-1,3,4-trione (IIIc). Yield 92%, mp 195–197°C (from EtOAc). IR spectrum, ν, cm^{-1}: 3175 (NH), 3098 br (NH, H-bonded), 1688 (C$^{3'}$=O, C^4=O), 1653 (C^1=O), 1608 (C^3=O, H-bonded). ^{1}H NMR spectrum, δ, ppm: 1.43 s (6H, Me), 3.27 s (3H, NMe), 3.32 s (3H, MeO), 5.82 s (1H, CH), 6.99–7.81 m (12H, H$_{\text{arom}}$), 12.04 s (1H, N$^{4'}$H), 14.47 s (1H, N$^{1'}$H). ^{13}C NMR spectrum, δ$_\text{C}$, ppm: 21.93 ($3''$-CH$_3$), 29.82 (CH$_3$N), 48.11 (C$^{3''}$), 109.14 (C^5), 115.41–146.39 (C$_{\text{arom}}$), 154.81 (C$^{3'}$), 173.74 (C^4), 183.57 (C^3), 191.11 (C^1). Found, %: C 71.30; H 5.26; N 8.00. C$_{31}$H$_{27}$N$_3$O$_5$. Calculated, %: C 71.39; H 5.22; N 8.06.

(2*Z*)-1-(4-Chlorophenyl)-2-[3-oxo-3,4-dihydroquinoxalin-2(1*H*)-ylidene]-5-(1,3,3-trimethyl-2,3-dihydro-1*H*-indol-2-ylidene)pentane-1,3,4-trione (IIId). Yield 90%, mp 191–192°C (from dichloroethane). IR spectrum, ν, cm^{-1}: 3175 (NH), 3093 br (NH, H-bonded), 1686 (C$^{3'}$=O, C^4=O), 1651 (C^1=O), 1605 (C^3=O, H-bonded). ^{1}H NMR spectrum, δ, ppm: 1.43 s (6H, Me), 3.27 s (3H, NMe), 5.82 s (1H, CH), 7.02–7.81 m (12H, H$_{\text{arom}}$), 12.04 s (1H, N$^{4'}$H), 14.47 s (1H, N$^{1'}$H). Found, %: C 68.38; H 4.66; N 7.83. C$_{30}$H$_{24}$ClN$_3$O$_4$. Calculated, %: C 68.50; H 4.60; N 7.99.

(2*Z*)-1-(4-Bromophenyl)-2-[3-oxo-3,4-dihydroquinoxalin-2(1*H*)-ylidene]-5-(1,3,3-trimethyl-2,3-dihydro-1*H*-indol-2-ylidene)pentane-1,3,4-trione (IIIe). Yield 89%, mp 175–177°C (from dichloroethane). IR spectrum, ν, cm^{-1}: 3175 (NH), 3094 br (NH, H-bonded), 1679 (C$^{3'}$=O, C^4=O), 1651 (C^1=O), 1609 (C^3=O, H-bonded). ^{1}H NMR spectrum, δ, ppm: 1.43 s (6H, Me), 3.28 s (3H, NMe), 5.83 s (1H, CH), 7.00–7.94 m (12H, H$_{\text{arom}}$), 12.04 s (1H, N$^{4'}$H), 14.46 s (1H, N$^{1'}$H). Found, %: C 63.09; H 4.36; N 7.24. C$_{30}$H$_{24}$N$_3$O$_4$Br. Calculated, %: C 63.17; H 4.24; N 7.37.

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