ISSN 1070-4280, Russian Journal of Organic Chemistry, 2012, Vol. 48, No. 4, pp. 616–617. © Pleiades Publishing, Ltd., 2012.
Original Russian Text © V.L. Gein, R.O. Dyrenkov, N.A. Kornienko, M.I. Vakhrin, P.A. Slepukhin, 2012, published in Zhurnal Organicheskoi Khimii, 2012, Vol. 48, No. 4, pp. 616–617.

SHORT COMMUNICATIONS

Formation of Alkyl 1-Methyl-3,9-dioxo-2-phenyl-2,3,4,9-tetrahydro-1*H*-pyrrolo[3,4-*b*]quinoline-1-carboxylates by Thermolysis of Alkyl 1,5-Diaryl-4-methyl-2,3,6-trioxo-1,2,3,4,5,6-hexahydropyrrolo[3,4-*b*]pyrrole-4-carboxylates

V. L. Gein[a], R. O. Dyrenkov[a], N. A. Kornienko[a], M. I. Vakhrin[a], and P. A. Slepukhin[b]

[a] *Perm State Pharmaceutical Academy, ul. Polevaya 2, Perm, 614000 Russia*
e-mail: geinvl48@mail.ru

[b] *Postovskii Institute of Organic Synthesis, Ural Division, Russian Academy of Sciences, ul. S. Kovalevskoi/Akademicheskaya 20/22, Yekaterinburg, 620990 Russia*

Received June 15, 2011

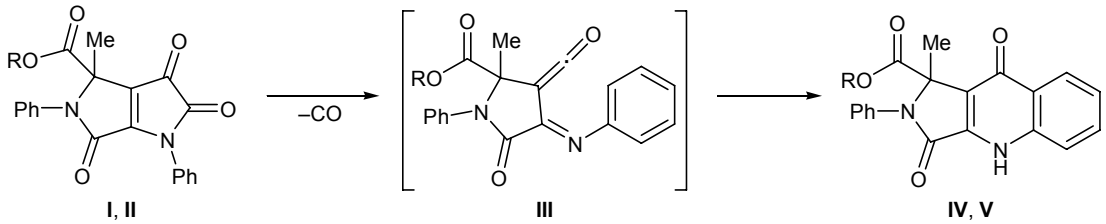
DOI: 10.1134/S1070428012040306

Several examples of thermal decomposition of pyrrolediones have been reported. For instance, cyclization of *N*-arylimidoyl(acyl)ketenes to substituted quinolinones was described, and the acyl carbonyl group was not involved in the process [1, 2].

We were the first to study thermolysis of pyrrole-2,3-dione fused to a dihydropyrrole ring. Heating of compounds **I** and **II** in boiling anhydrous decane over a period of 30–60 min led to the formation of alkyl 1-methyl-3,9-dioxo-2-phenyl-2,3,4,9-tetrahydro-1*H*-pyrrolo[3,4-*b*]quinoline-1-carboxylates **IV** and **V**. The products were isolated as colorless crystalline substances which were soluble in DMF, DMSO, and hot acetic acid. The IR spectra of **IV** and **V** contained absorption bands due to stretching vibrations of the ester (1728–1750 cm^{-1}), lactam (1720–1728 cm^{-1}), and ketone carbonyl groups (1624–1628 cm^{-1}) and amino group (3210 cm^{-1}). Compounds **IV** and **V** showed in the ^1H NMR spectra signals from aromatic protons, a triplet from the methyl group in position *1* at δ 1.72–1.73 ppm, a singlet from the ester methoxy group at δ 3.63 ppm (**IV**) or a triplet a quartet at δ 1.08 and 4.12 ppm from the ethoxy group (**V**), and a singlet from the NH proton at δ 12.91–13.04 ppm. The structure of compound **V** was unambiguously determined by X-ray analysis of its single crystal obtained by slow crystallization from acetic acid (see figure).

Presumably, thermal decarbonylation of fused pyrroledione **I** or **II** generates unsymmetrical di(imidoyl)-ketene **III** which is stabilized via CH-acylation by the ketene fragment of the *ortho*-position in the phenyl substituent.

Methyl 1-methyl-3,9-dioxo-2-phenyl-2,3,4,9-tetrahydro-1*H*-pyrrolo[3,4-*b*]quinoline-1-carboxylate (IV). A mixture of 1.0 mmol of compound **I** in 30 ml of anhydrous decane was heated for 30–60 min under reflux. The mixture was cooled, and the precipitate was filtered off. Yield 2.1 g (55%), mp 265–267°C (from acetic acid). IR spectrum, ν, cm^{-1}: 3210 (N–H), 1750 (C=O), 1728 (C^3=O), 1628 (C^9=O). ^1H NMR spectrum, δ, ppm: 1.72 s (3H, CH_3), 3.63 s (3H, OCH_3), 7.23–8.14 m (9H, H_{arom}), 12.91 s (1H,

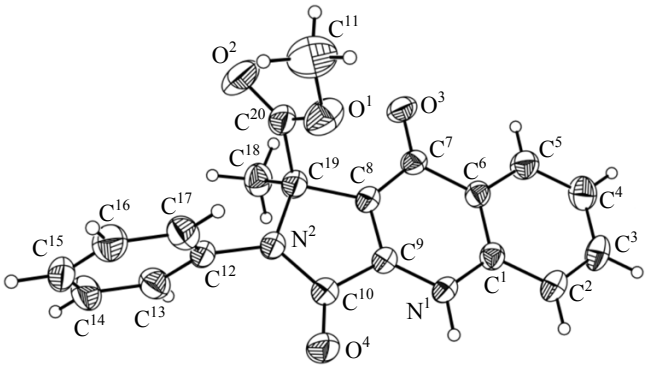


I, **IV**, R = Me; **II**, **V**, R = Et.

NH). Found, %: C 68.19; H 5.61; N 8.47. $C_{20}H_{16}N_2O_4$. Calculated, %: C 68.08; H 5.51; N 8.40.

Ethyl 1-methyl-3,9-dioxo-2-phenyl-2,3,4,9-tetrahydro-1*H*-pyrrolo[3,4-*b*]quinoline-1-carboxylate (V) was synthesized in a similar way. Yield 2.3 g (60%), mp 273–275°C (from acetic acid). IR spectrum, ν, cm^{-1}: 3210 (N–H), 1755 (C=O), 1720 (C^3=O), 1624 (C^9=O). ^{1}H NMR spectrum, δ, ppm: 1.08 t (3H, C**H**$_3$CH$_2$, J = 7.1 Hz), 1.73 s (3H, CH_3), 4.12 q (2H, C**H**$_2$CH$_3$, J = 7.1 Hz), 7.23–8.20 m (9H, H_{arom}), 13.04 s (1H, NH). Found, %: C 69.69; H 5.11; N 7.80. $C_{21}H_{18}N_2O_4$. Calculated, %: C 69.60; H 5.01; N 7.73.

The IR spectra were recorded on a Specord M-80 spectrometer from samples dispersed in mineral oil. The ^{1}H NMR spectra were measured on Bruker DRX-300 and DRX-500 spectrometers from solutions in DMSO-d_6 using TMS as internal reference. X-Ray analysis was performed on an Xcalibur S automatic four-circle diffractometer according to standard procedure [MoK_α irradiation, 295(2) K, ω/2θ scanning]. The structure was solved and refined using SHELXTL [3]. The crystallographic data for compound **V** were deposited to the Cambridge Crystallographic Data Centre (entry no. CCDC 873442) and are available at *www.ccdc.cam.ac.uk/data_request/cif* upon request.



Structure of the molecule of ethyl 1-methyl-3,9-dioxo-2-phenyl-2,3,4,9-tetrahydro-1*H*-pyrrolo[3,4-*b*]quinoline-1-carboxylate (**V**) according to the X-ray diffraction data. Non-hydrogen atoms are shown as thermal vibration ellipsoids with a probability of 50%.

REFERENCES

1. Sano, T.J., *Synth. Org. Chem. Jpn*., 1984, vol. 42, p. 340.
2. Maslivets, A.N., Krasnykh, O.P., Smirnova, L.I., and Andreichikov, Yu.S., *Zh. Org. Khim*., 1989, vol. 25, p. 1045.
3. Sheldrick, G.M., *Acta Crystallogr., Sect. A*, 2008, vol. 64, p. 112.