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Five-Membered 2,3-Dioxoheterocycles: LXXXVII.* [4+2]-Cycloaddition of Alkyl Vinyl Ethers and 3,4-Dihydro-2*H*-pyran to 4,5-Diaroyl-1*H*-pyrrole-2,3-diones

P. S. Silaichev[a,b], N. V. Kudrevatykh[b], and A. N. Maslivets[a,b]

[a]*Institute of Natural Sciences at Perm State University, Perm, 614990 Russia*
e-mail: koh2@psu.ru
[b]*Perm State University, Perm, Russia*

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Abstract—1-Aryl-4,5-diaroyl-1*H*-pyrrole-2,3-diones react with alkyl vinyl ethers and 3,4-dihydro-2*H*-pyran affording 1,4-diaryl-7a-aroyl-6-ethoxy-7,7a-dihydropyrano[4,3-*b*]pyrrole-2,3(1*H*,6*H*)-diones and 1,4-diaryl-9b-aroyl-1,7,8,9,9a-hexahydro-5a*H*-pyrano[3',2':5,6]pyrano[4,3-*b*]-pyrrole-2,3-diones respectively.

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1*H*-Pyrrole-2,3-diones were found to be very active in Diels–Alder reactions [2, 3]. The conjugated system C^5=C^4–C=O of 4-benzoyl-1-phenyl-5-ethoxycarbonyl-1*H*-pyrrole-2,3-dione enters as a diene into [4+2]-cycloaddition with a C=C bond of polar olefins resulting in a regioselective building of a pyrano[4,3-*b*]pyrrole heterocyclic system [4, 5]. 1-Aryl-4,5-diaroyl-1*H*-pyrrole-2,3-dione similarly reacted with styrene, and the structure of the formed 1,4-diaryl-7a-aroyl-6-phenyl-7,7a-dihydropyrano[4,3-*b*]pyrrole-2,3(1*H*,6*H*)-diones was proved for the first time by XRD study [6]. The reactions of alkoxyethylenes with 4,5-diaroyl-1*H*-pyrrole-2,3-diones have not been examined before.

Aiming at the investigation of the effect of an aroyl fragment in the position *5* of 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** [6, 7] with alkyl vinyl ethers **IIa, IIb** and 3,4-dihydro-2*H*-pyran (**III**).

The heating of 1-aryl-4,5-diaroyl-1*H*-pyrrole-2,3-diones **Ia–Ig** with alkyl vinyl ethers **IIa, IIb** in a ratio 1:1.5 in anhydrous benzene for 20–30 min an with 3,4-dihydro-2*H*-pyran (**III**) in a ratio 1:1.5 in toluens for 60–70 min (till the disappearance of the bright red color of pyrrolediones) furnished 1,4-diaryl-7a-aroyl-6-alkoxy-7,7a-dihydropyrano[4,3-*b*]pyrrole-2,3(1*H*,6*H*)-diones **IVa–IVd** and 1,4-diaryl-9b-aroyl-1,7,8,9,9a-hexahydro-5a*H*-pyrano[3',2':5,6]pyrano[4,3-*b*]pyrrole-2,3-diones **Va–Ve** respectively.

Compounds **IVa–IVd**, **Va–Ve** are light-yellow or colorless crystalline substances of a high melting point, readily soluble in common organic solvents, nsoluble in alkanes and water.

The IR spectra of compounds **IVa–IVd**, **Va–Ve** contain the bands of the stretching vibrations of lactam C^2=O and keto C^3=O carbonyl groups in the form of a single broad or two narrow bands in the region 1703–1736 cm^{-1}, and of the aroyl carbonyl group at 1674–1692 cm^{-1}. The position of absorption bands of C^2=O and C^3=O groups in the IR spectra of compounds **IVa–IVd**, **Va–Ve** coincides with their position

(1720–1730 cm^{-1}) in the IR pectra of (3*R**,4a*R**)-4,4a,6,7-tetrahydro-6,7-dioxo-1,5-diphenyl-3-ethoxy-4a-ethoxycarbonyl-5*H*-pyrano[4,3-*b*]pyrrole (**VI**) and (5a*R**,9a*S**,9b*R**)-2,3,8,9,9a,9b-hexahydro-2,3-dioxo-1,4-diphenyl-9b-ethoxycarbonyl-1*H*-pyrano-[3',2':5,6] pyrano[4,3-*b*]pyrrole (**VII**) [4].

In the ^{1}H NMR spectra of compounds **IVa–IVd** alongside the signals of the protons of aromatic rings, methyl and alkoxy groups doublet of doublets signals of the methine proton H^6 (5.64–5.83 ppm) are present, and also of the methylene protons C^7H_2 (2.37–3.34 ppm) giving a typical *ACX* system. The position and multiplicity of

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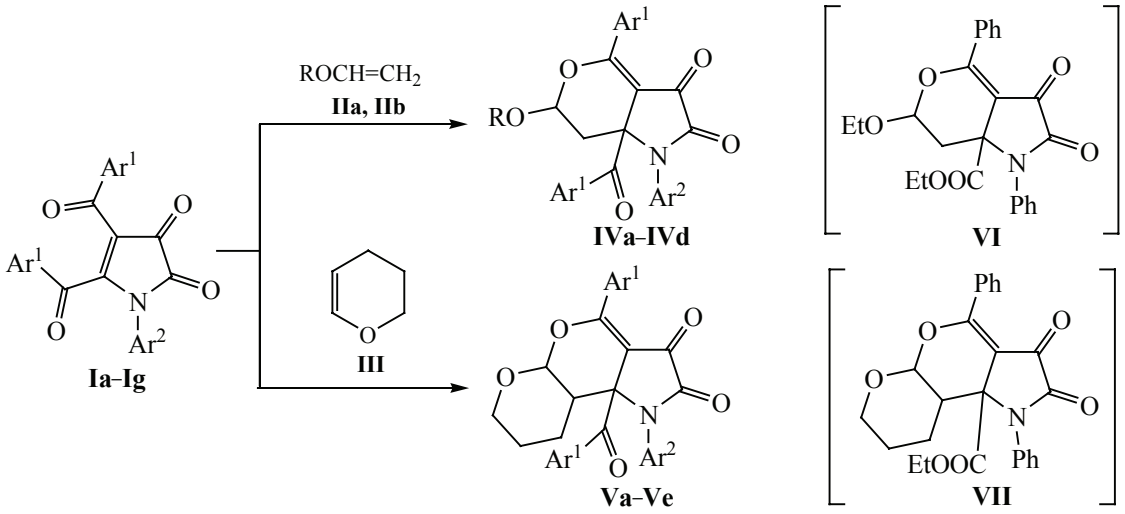

I, Ar^1 = Ph, Ar^2 = C_6H_4Me-4 (**a**); Ar^1 = Ar^2 = C_6H_4Me-4 (**b**); Ar^1 = C_6H_4Me-4, Ar^2 = Ph (**c**); Ar^1 = $C_6H_3Me_2$-2,5, Ar^2 = Ph (**d**); Ar^1 = $C_6H_3Me_2$-2,5, Ar^2 = C_6H_4OMe-4 (**e**); Ar^1 = C_6H_4Me-4, Ar^2 = C_6H_4OMe-4 (**f**); Ar^1 = $C_6H_3Me_2$-2,5, Ar^2 = C_6H_4Me-4 (**g**); **II**, R = Et (**a**), Bu (**b**); **IV**, Ar^1 = C_6H_4Me-4, R = Et, Ar^2 = Ph (**a**); Ar^1 = Ar^2 = C_6H_4Me-4, R = Et (**b**); Ar^1 = Ar^2 = C_6H_4Me-4, R = Bu (**c**); Ar^1 = $C_6H_3Me_2$-2,5, Ar^2 = C_6H_4OMe-4, R = Et (**d**); **V**, Ar^1 = Ph, Ar^2 = C_6H_4Me-4 (**a**); Ar^1 = Ar^2 = C_6H_4Me-4 (**b**); Ar^1 = C_6H_4Me-4, Ar^2 = C_6H_4OMe-4 (**c**); Ar^1 = $C_6H_3Me_2$-2,5, Ar^2 = Ph (**d**); Ar^1 = $C_6H_3Me_2$-2,5, Ar^2 = C_6H_4Me-4 (**e**).

proton signals belonging to H^6 and C^7H_2 in the ^1H NMR spectra of compounds **IVa–IVd** are very simlar to those of the protons H^6 (d.d, 1H, 5.86 ppm) and C^7H_2 (d.d, 2H, 1.98–3.06 ppm) of pyrano-[3',2':5,6]pyrano[4,3-*b*]pyrrole fragment in the ^1H NMR spectrum of compound **VI** [4].

In the ^1H NMR spectra of compounds **Va–Ve** alongside the signals of the protons of aromatic rings and the groups attached thereto the signals are present of the methylene protons C^8H_2 and C^9H_2 (1.14–1.80 ppm), a multiplet of the methine proton H^{9a} (3.14–3.21 ppm), a multiplet of the methylene protons C^7H_2 (3.81–3.86 ppm), and a doublet of the methine proton H^{5a} (5.94–6.10 ppm). The position and multiplicity of the signals of thes protons in the ^1H NMR spectra of compounds **Va–Ve** are very similar to those of protons C^8H_2 and C^9H_2 (m, 4H, 1.41–1.73 ppm), H^{9a} (m, 1H, 2.97 ppm), C^7H_2 (m, 2H, 3.88–3.90 ppm), and H^{5a} (d, 1H, 6.29 ppm) of pyrano-[3',2':5,6]pyrano[4,3-*b*]pyrrole fragment in the ^1H NMR spectrum of compound **VII** [4].

In the ^{13}C NMR spectrum of compound **Vd** alongside the signals of the carbon atoms of aromatic substituents, methyl and methylene groups signals are observed of the carbon atoms of the aroyl carbonyl group at 202.80 ppm, of keto (C^3=O) and lactam (C^2=O) carbonyl groups of the pyrroledione ring at 177.20 and 161.94 ppm respectively, and also the signals of carbon atoms in the positions *5*a, *9*a, and *9*b of the pyrano[3',2':5,6]pyrano[4,3-*b*]pyrrole-2,3-dione fragment at 98.20, 32.01, and 68.89 ppm respectively, very similar to the position of the carbon atoms in the positions *2*, *3*, *5*a, *9*a, and *9*b in the pyrano[3',2':5,6] pyrano[4,3-*b*]pyrrole-2,3-dione fragment in the ^{13}C NMR spectrum of compound **VII** [4].

The formation of compounds **IVa–IVd**, **Va–Ve** is evidently due to the involvement of the conjugated system of bonds O=C–C^4=C^5 belonging to pyrrolediones **Ia–Ig** in the thermally initiated [4+2]-cycloaddition to a polarized C=C bond of alkoxyethylenes **IIa, IIb, III**.

EXPERIMENTAL

IR spectra of compounds obtained were recorded on a spectrophotometer FSM-1201. NMR spectra were registered on a spectrometer Bruker AM-400 [operating frequencies 400 (^1H) and 100 (^{13}C) MHz] in DMSO-d_6, internal reference TMS. The homogeneity of the compounds synthesized was proved by TLC on Silufol plates, eluents benzene–ethyl acetate, 5:1, ethyl acetate, development in iodine vapor or under UV irradiation.

4-(4-Tolyl)-7a-(4-toluoyl)-1-phenyl-6-ethoxy-7,7a-dihydropyrano[4,3-*b*]pyrrole-2,3(1*H*,6*H*)-dione (IVa). To a solution of 1.0 mmol of compound **Ic** in 50 ml of anhydrous benzene was added a solution of 1.5 mmol of ethyl vinyl ether (**IIa**) in 5 ml of anhydrous benzene, the mixture was heated for 25 min at 60–70°C, cooled, the separated precipitate was filtered off. Yiled 89%, mp 189–190°C (benzene–hexane, 1 : 1). IR spectrum, cm^{-1}: 1723 (C^2=O, C^3=O), 1674 (C^{7a}–C=O). ^1H NMR spec-

trum, δ, ppm: 1.25 t (3H, Me, *J* 7.2 Hz), 2.37 s (3H, Me), 2.41 s (3H, Me), 2.42 d.d (1H, C^7H_2, *J* 12.4, 8.8 Hz), 3.04 d.d (1H, C^7H_2, *J* 12.4, 5.2 Hz), 3.81 s (3H, OMe), 3.84 m (1H, OCH_2), 4.08 m (1H, OCH_2), 5.83 d.d (1H, H^6, *J* 8.8, 5.2 Hz), 6.95–7.29 group of signals (10H, C_6H_4 + $2C_6H_3$). Found, %: C 74.79; H 5.67; N 2.87. $C_{30}H_{27}NO_5$. Calculated, %: C 74.83; H 5.65; N 2.91.

Compounds **IVb–IVd** were similarly prepared.

1,4-Di(4-tolyl)-7a-(4-toluoyl)-6-ethoxy-7,7a-dihydropyrano[4,3-*b*]pyrrole-2,3(1*H*,6*H*)-dione (IVb). Yield 92%, mp 189–190°C (benzene–petroleum ether, 1:1). IR spectrum, cm^{-1}: 1736 (C^2=O), 1727 (C^2=O), 1680 (C^{7a}–C=O). ^1H NMR spectrum, δ, ppm: 1.25 t (3H, Me, *J* 7.0 Hz), 2.31 s (3H, Me), 2.37 s (3H, Me), 2.37 d.d (1H, C^7H_2, *J* 12.8, 8.8 Hz), 2.41 s (3H, Me), 3.05 d.d (1H, C^7H_2, *J* 12.8, 4.9 Hz), 3.84 m (1H, OCH_2) 4.08 m (1H, OCH_2), 5.82 d.d (1H, H^6, *J* 8.8, 4.9 Hz), 6.97–7.72 group of signals (12H, $3C_6H_4$). Found, %: C 75.15; H 5.86; N 2.79. $C_{31}H_{29}NO_5$. Calculated, %: C 75.13; H 5.90; N 2.83.

6-Butoxy-1,4-di(4-tolyl)-7a-(4-toluoyl)-7,7a-dihydropyrano[4,3-*b*]pyrrole-2,3(1*H*,6*H*)-dione (IVc). Yield 78%, mp 150–151°C (benzene–petroleum ether, 1:1). IR spectrum, cm^{-1}: 1720 (C^2=O, C^3=O), 1684 (C^{7a}–C=O). ^1H NMR spectrum, δ, ppm: 0.92 t (3H, Me, *J* 7.2 Hz), 1.39 m (2H, CH_2), 1.60 m (2H, CH_2), 2.31 s (3H, Me), 2.37 s (3H, Me), 2.41 s (3H, Me), 3.04 d.d (1H, C^7H_2, *J* 12.4, 4.8 Hz), 3.34 d.d (1H, C^7H_2, *J* 12.4, 8.8 Hz), 3.78 m (1H, OCH_2), 4.03 m (1H, OCH_2), 5.80 d.d (1H, H^6, *J* 8.8, 4.8 Hz), 6.97–7.72 group of signals (12H, $3C_6H_4$). Found, %: C 75.71; H 6.31; N 2.63. $C_{33}H_{33}NO_5$. Calculated, %: C 75.69; H 6.35; N 2.67.

7a-(2,5-Dimethylbenzoyl)-4-(2,5-dimethyl-phenyl)-1-(4-methoxyphenyl)-6-ethoxy-7,7a-dihydropyrano[4,3-*b*]pyrrole-2,3(1*H*,6*H*)-dione (IVd). Yield 86%, mp 151–152°C (benzene–petroleum ether, 1:1). IR spectrum, cm^{-1}: 1721 (C^2=O, C^3=O), 1686 (C^{7a}–C=O). ^1H NMR spectrum, δ, ppm: 1.18 t (3H, Me, *J* 6.8 Hz), 2.04 s (3H, Me), 2.06 s (3H, Me), 2.18 s (3H, Me), 2.27 s (3H, Me), 2.38 d.d (1H, C^7H_2, *J* 12.8, 9.6 Hz), 2.96 d.d (1H, C^7H_2, *J* 12.8, 4.2 Hz), 3.77 m (1H, OCH_2) 3.81 s (3H, OMe), 3.94 m (1H, OCH_2), 5.64 d.d (1H, H^6, *J* 9.6, 4.2 Hz), 6.95–7.29 group of signals (10H, C_6H_4 + $2C_6H_3$). Found, %: C 73.41; H 6.18; N 2.63. $C_{33}H_{33}NO_6$. Calculated, %: C 73.45; H 6.16; N 2.60.

9b-Benzoyl-1-(4-tolyl)-4-phenyl-1,7,8,9,9a-hexahydro-5a*H*-pyrano[3',2':5,6]pyrano[4,3-*b*]pyrrole-2,3-dione (Va). To a solution of 1.0 mmol of compound **Ia** in 25 ml of anhydrous toluene was added a solution of 1.2 mmol of 3,4-dihydro-2*H*-pyran (**III**) in 5 ml of toluene, the mixture was boiled for 1 h, cooled, the separated precipitate was filtered off. Yield 84%, mp 235–236°C (toluene). IR spectrum, cm^{-1}: 1728 (C^2=O), 1715 (C^3=O), 1690 (C^{9b}–C=O). ^1H NMR spectrum, δ, ppm: 1.20–1.80 group of signals (4H, $2CH_2$), 2.34 s (3H, Me), 3.17 m (1H, H^{9a}), 3.86 m (2H, C^7H_2), 6.10 d (1H, H^{5a}, *J* 3.6 Hz), 7.23–7.77 group of signals (14H, $2C_6H_5$, C_6H_4). Found, %: C 75.10; H 5.24; N 2.89. $C_{30}H_{25}NO_5$. Calculated, %: C 75.14; H 5.25; N 2.92.

Compounds **Vb–Ve** were similarly prepared.

1,4-Di(4-tolyl)-9b-(4-toluoyl)-1,7,8,9,9a-hexahydro-5a*H*-pyrano[3',2':5,6]pyrano[4,3-*b*]pyrrole-2,3-dione (Vb). Yield 81%, mp 220–221°C (toluene). IR spectrum, cm^{-1}: 1719 (C^2=O), 1703 (C^3=O), 1682 (C^{9b}–C=O). ^1H NMR spectrum, δ, ppm: 1.18–1.73 group of signals (4H, $2CH_2$), 2.33 s (3H, Me), 2.34 s (3H, Me), 2.42 s (3H, Me), 3.15 m (1H, H^{9a}), 3.84 m (2H, C^7H_2), 6.08 d (1H, H^{5a}, *J* 3.5 Hz), 7.19–7.70 group of signals (12H, $3C_6H_4$). Found, %: C 75.70; H 5.73; N 2.73. $C_{32}H_{29}NO_5$. Calculated, %: C 75.72; H 5.76; N 2.76.

1-(4-Methoxyphenyl)-4-(4-tolyl)-9b-toluoyl-1,7,8,9,9a-hexahydro-5a*H*-pyrano[3',2':5,6]pyrano[4,3-*b*]pyrrole-2,3-dione (Vc). Yield 91%, mp 221–223°C (toluene). IR spectrum, cm^{-1}: 1703 (C^2=O, C^3=O), 1680 (C^{9b}–C=O). ^1H NMR spectrum, δ, ppm: 1.14–1.80 group of signals (4H, $2CH_2$), 2.35 s (3H, Me), 2.42 s (3H, Me), 3.14 m (1H, H^{9a}), 3.78 s (3H, OMe), 3.85 m (2H, C^7H_2), 6.03 d (1H, H^{5a}, *J* 3.2 Hz), 7.03–7.70 group of signals (12H, $3C_6H_4$). Found, %: C 73.38; H 5.54; N 2.64. $C_{32}H_{29}NO_6$. Calculated, %: C 73.41; H 5.58; N 2.68.

9b-(2,5-Dimethylbenzoyl)-4-(2,5-dimethylphenyl)-1-phenyl-1,7,8,9,9a-hexahydro-5a*H*-pyrano-[3',2':5,6]pyrano[4,3-*b*]pyrrole-2,3-dione (Vd). Yield 79%, mp 217–218°C (toluene). IR spectrum, cm^{-1}: 1727 (C^2=O), 1717 (C^3=O), 1692 (C^{9b}–C=O). ^1H NMR spectrum, δ, ppm: 1.30–1.70 group of signals (4H, $2CH_2$), 2.09 s (3H, Me), 2.10 s (3H, Me), 2.28 s (3H, Me), 2.30 s (3H, Me), 3.21 m (1H, H^{9a}), 3.82 m (2H, C^7H_2), 5.96 d (1H, H^{5a}, *J* 5.1 Hz), 6.81–7.58 group of signals (11H, Ph, $2C_6H_3$). ^{13}C NMR spectrum, δ, ppm: 17.14 (C^9), 18.78 (Me), 18.96 (Me), 20.13 (Me), 20.23 (Me), 22.71 (C^8), 32.01 (C^{9a}), 61.39 (C^7), 68.89 (C^{9b}), 98.20 (C^{5a}), 122.50–137.22 group of signals (C^{Ar}, C^{3a}), 161.94 (C^2), 165.16 (C^4), 177.20 (C^3), 202.80 (C^{9b}–CO). Found, %: 75.95; H 5.95; N 2.67. $C_{33}H_{31}NO_5$. Calculated, %: C 75.99; H 5.99; N 2.69.

9b-(2,5-Dimethylbenzoyl)-4-(2,5-dimethylphenyl)-1-(4-tolyl)-1,7,8,9,9a-hexahydro-5a*H*-pyrano[3',2':5,6]-pyrano[4,3-*b*]pyrrole-2,3-dione (Ve). Yield 77%, mp 203–205°C (toluene). IR spectrum, cm^{-1}: 1723 (C^2=O, C^3=O), 1692 (C^{9b}–C=O). ^{1}H NMR spectrum, δ, ppm: 1.30–1.70 group of signals (4H, $2CH_2$), 2.08 s (6H, 2Me), 2.28 s (3H, Me), 2.30 s (3H, Me), 2.37 s (3H, Me), 3.18 m (1H, H^{9a}), 3.81 m (2H, C^7H_2), 5.94 d (1H, H^{5a}, *J* 3.0 Hz), 6.79–7.38 group of signals (10H, C_6H_4, $2C_6H_3$). Found, %: C 76.20; H 6.19; N 2.58. $C_{34}H_{33}NO_5$. Calculated, %: C 76.24; H 6.21; N 2.61.

REFERENCES

1. Bubnov, N.V., Denislamova, E.S., Silaichev, P.S., Slepukhin, P.A., and Maslivets, A.N., *Zh. Org. Khim*., 2012, vol. 48, p. 697.
2. Maslivets, A.N. and Mashevskaya, I.V., *2,3-Digidro-2,3-pirroldiony* (2,3-Dihydropyrrole-2,3-diones), Perm: Izd. Perm. Gos. Univ., 2005, p. 63.
3. Sano, T., *J. Synth. Org. Chem.,* 1984, vol. 42, p. 340.
4. Horiguchi, Y., Sano, T., and Tsuda, Y., *Chem. Pharm. Bull.,* 1996, vol. 44, p. 670.
5. Horiguchi, Y., Sano, T., Kiuchi, F., and Tsuda, Y., *Chem. Pharm. Bull.,* 1996, vol. 44, p. 681.
6. Silaichev, P.S., Kudrevatykh, N.V., Z.G.Aliev, and Maslivets, A.N., *Zh. Org. Khim*., 2012, vol. 48, p. 263.
7. Silaichev, P.S., Kudrevatykh, N.V., and Maslivets, A.N., *Zh. Org. Khim*., 2012, vol. 48, p. 259.