ISSN 1070-4280, Russian Journal of Organic Chemistry, 2012, Vol. 48, No. 2, pp. 249–252. © Pleiades Publishing, Ltd., 2012.
Original Russian Text © P.S. Silaichev, N.V. Kudrevatykh, A.N. Maslivets, 2012, published in Zhurnal Organicheskoi Khimii, 2012, Vol. 48, No. 2, pp. 259–262.

Five-Membered 2,3-Dioxoheterocycles: LXXXIII.* Synthesis and Thermolysis of 1-Aryl-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*

Received May 19, 2011

Abstract—The reaction of (*Z*)-2-amino-1,4-diarylbut-2-en-1,4-diones with oxalyl chloride led to the formation of 1-aryl-4,5-diaroyl-1*H*-pyrrole-2,3-diones that at the thermal decarbonylation gave aroyl(*N*-arylimidoyl)ketenes which underwent stabilization by molecular cyclization into 2,3-diaroylquinolin-4(1*H*)-ones.

DOI: 10.1134/S1070428012020145

The thermolysis of 4-benzoyl-1,5-diphenyl-1*H*-pyrrole-2,3-dione leads to its decarbonylation [elimination of a molecule of carbon(II) oxide] and to the generation of a substituted benzoyl(*N*-phenylimidoyl)ketene that suffers an intramolecular cyclization through the acylation by the ketene fragment of the CH group in the *ortho*-position of the benzene ring at the nitrogen atom giving 2-phenyl-3-benzoyl-quinolin-4(1*H*)-one [2]. The formation as an intermediate of the imidoylketene stable at the temperature below –70°C we succeeded to detect at the flash-pyrolysis of this pyrroledione [3]. The thermolysis of 1-aryl-4-aroyl-5-methoxycarbonyl-1*H*-pyrrole-2,3-diones proceeded also with CO elimination and the formation of a substituted aroyl(N-arylimidoyl)-ketene undergoing the intramolecular cyclization into 3-aroyl-2-methoxycarbonylquinolin-4(1*H*)-ones [4].

With the goal to investigate the influence of the introduction of an aroyl fragment into the position *5* of the 1-aryl-4-aroyl-substituted 1*H*-pyrrole-2,3-diones on the direction of the stabilization of the generated at their thermal decarbonylation substituted aroyl(*N*-arylimidoyl)ketenes we synthesized 1-aryl-4,5-diaroyl-1*H*-pyrrole-2,3-diones **Ia–Ie** and studied their thermolysis. The structural features of the substituted aroyl(*N*-arylimidoyl)ketenes **IIa–IIe** generated by the thermolysis of these pyrrolediones suggest that in their stabilization besides the above described way may arise other routes of intramolecular cyclization, for instance, involving the *ortho*-position of the benzene ring of the “new” aroyl fragment along the scheme analogous to the stabilization of substituted bis(imidoyl)ketenes [5].

Initial compounds for the synthesis of pyrrolediones **Ia–Ie**, (*Z*)-1,4-diaryl-2-arylaminobut-2-ene-1,4-diones **IIIa, IIIb**, were obtained by the reaction of bis(2,5-dimethylbenzoyl)acetylene with anilines, and enamines **IIIc, IIId** [6] and enamine **IIIe** [7] were synthesized by known procedures.

Compounds **IIIa, IIIb** are orange crystalline substances of low melting points, readily soluble in common organic solvents, sparingly soluble in alkanes, insoluble in water.

The IR spectra of compounds **IIIa, IIIb** contain the absorption bands of stretching vibrations of NH group as a wide band in the region 3150–3160 cm^{-1}, of the “free” aroyl carbonyl group (1665–1678 cm^{-1}), and of the aroyl carbonyl group involved in the formation of intramolecular hydrogen bonds (1600–1605 cm^{-1}).

In the ^{1}H NMR spectra of compounds **IIIa, IIIb** solutions in DMSO-d_6 alongside the signals of the

---

*Communication LXXXII see [1].

protons of the aromatic rings and the groups attached to them a singlet of a vinyl proton (5.70–5.78 ppm) and a broadened singlet of the NH group involved in the formation of intramolecular hydrogen bonds (downfield at 12.04–12.06 ppm) are observed.

The spectral characteristics of compounds **IIIa,IIIb** show that they exist in the crystalline state and in solution in the form of *Z*-isomers with a strong intramolecular hydrogen bond of an H-chelate type between the NH and aroyl group as is characteristic of this class substances [4, 6, 7].

At boiling the solution of enamines **IIIa–IIIe** and oxalyl chloride (1:1.1) in anhydrous benzene over 70–80 min (till the end of HCl liberation) we obtained the desired 1-aryl-4,5-diaroyl-1*H*-pyrrole-2,3-diones **Ia–Ie**. In the preparation and crystallization of pyrrolediones thoroughly dried solvents and freshly distilled oxalyl chloride should be used: In this case the synthesis proceeds cleanly, and pyrrolediones **Ia–Ie** form in good yield.

Pyrrolediones **Ia–Ie** are orange or bright red crystalline substances of high melting point melting with decomposition, readily soluble in common organic solvents, DMF, and DMSO, insoluble in alkanes, reacting with water and alcohols, decolorizing at storage due to thereaction with air moisture.

The IR spectra of compounds **Ia–Ie** contain absorption bands of the stretching vibrations of lactam amd ketone carbonyl groups of the pyrroledione ring (1770–1779 and 1715–1738 cm^{-1} respectively), and also the carbonyl groups bands of the aroyl substituents (1636–1678 cm^{-1}).

Heating of 1-aryl-4,5-diaroyl-1*H*-pyrrole-2,3-diones **Ia–Ie** in an inert aprotic solvent (Dowtherm A) at 210–220°C for 15–20 min (till the end of CO bubbles liberation) led to the formation in good yields of 2,3-diaroylquinolin-4(1*H*)-ones **IVa–IVe**.

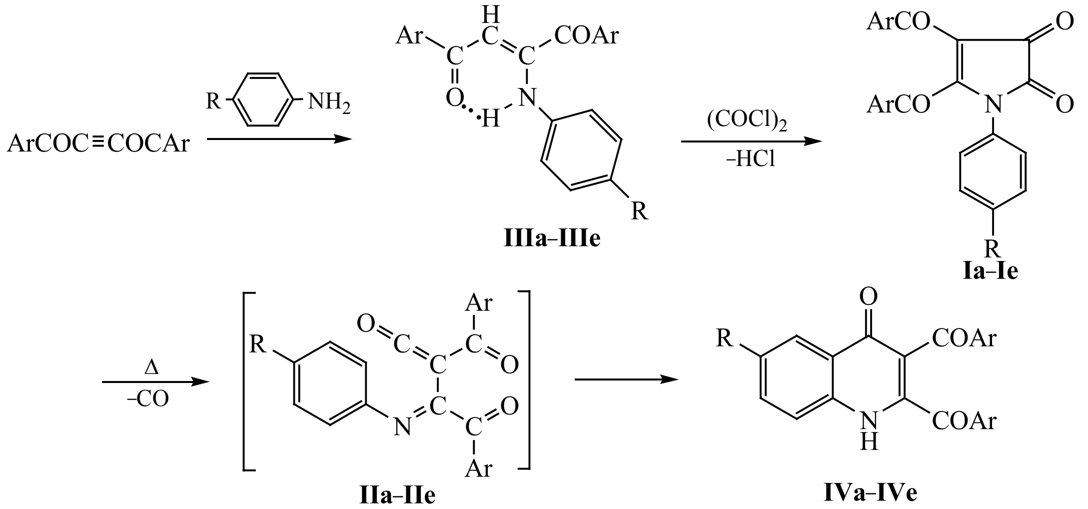
Compounds **IVa–IVe** are colorless crystalline substances of high melting points melting with decomposition, readily soluble in DMF and DMSO, sparingly soluble in common organic solvents, insoluble in water and alkanes.

The IR spectra of quinolinones **IVa–IVe** contain the absorption bands of stretching vibrations of NH group as a wide band in the region 3200–3265 cm^{-1}, of carbonyl keto groups of the aroyl substituents, and of carbonyl group of the quinolone ring as one or two bands in the region 1635–1682 Cm^{-1}.

In the ^{1}H NMR spectra of quinolinones **IVa–IVe** alongside the signals of the protons of the aromatic rings and the groups attached to them a signal is present of the proton of the NH as a broadened singlet at 12.77–12.86 ppm.

Spectral characteristics of the quinolin-4(1*H*)-ones are fairly similar to those of the model substituted quinolin-4(1*H*)-ones [2, 4].

The formation of compounds **IVa–IVe** proceeds apparently through the primary cheletropic elimination of the CO molecule resulting in imidoylketenes **IIa–IId** which undergo the stabilization due to the acylation with the ketene fragment of the CH group in the *ortho*-



R = H (**a, c, e**), OMe (**b, d**); Ar = 2,5-Me$_2$C$_6$H$_3$ (**a, b**), Ph (**c, d**), 4-MeC$_6$H$_4$ (**e**).

position of the benzene ring at the nitrogen atom. Thus the introduction of an aroyl group in the position *5* of 1-aryl-4-aroyl-substituted 1*H*-pyrrole-2,3-diones did not change the stabilization direction of the substituted aroyl(N-arylimidoyl)ketenes generated at their thermal decarbonylation. The reaction proceeds along the previously described scheme [2-4].

EXPERIMENTAL

IR spectra of compounds obtained were recorded on a spectrophotometer FSM-1201, ^{1}H NMR spectra were registered on a spectrometer Bruker AM-400 (400 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-Bis(2,5-dimethylbenzoyl)-1-phenyl-1*H*-pyrrole-2,3-dione (Ia). To 0.01 mol of compound **IIIa** 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 213–214°C (decomp., benzene). IR spectrum, ν, cm^{-1}: 1779 (C^2=O), 1715 (C^3=O), 1663 (C^4–C=O), 1638 (C^5–C=O). ^{1}H NMR spectrum, δ, ppm: 2.13 s (3H, Me), 2.28 s (3H, Me), 2.32 s (3H, Me), 2.49 s (3H, Me), 7.06-7.43 group of signals (11H, Ph + 2C$_6$H$_3$). Found, %: C 76.83; H 5.35; N 3.22. $C_{28}H_{23}NO_4$. Calculated, %: C 76.87; H 5.30; N 3.20.

Compounds **Ib–Id** were obtained in a similar way.

4,5-Bis(2,5-dimethylbenzoyl)-1-(4-methoxyphenyl)-1*H*-pyrrole-2,3-dione (Ib). Yield 65%, mp 213–214°C (decomp., benzene). IR spectrum, ν, cm^{-1}: 1779 (C^2=O), 1717 (C^3=O), 1663 (C^4–C=O), 1636 (C^5–C=O). ^{1}H NMR spectrum, δ, ppm: 2.12 s (3H, Me), 2.26 s (3H, Me), 2.31 s (3H, Me), 2.49 s (3H, Me), 3.71 s (3H, OMe), 6.93–7.36 group of signals (10H, C$_6$H$_4$ + 2C$_6$H$_3$). Found, %: C 74.54; H 5.35; N 3.03. $C_{29}H_{25}NO_5$. Calculated, %: C 74.50; H 5.39; N 3.00.

4,5-Dibenzoyl-1-phenyl-1*H*-pyrrole-2,3-dione (Ic). Yield 69%, mp 216–217°C (decomp., benzene). IR spectrum, ν, cm^{-1}: 1772 (C^2=O), 1738 (C^3=O), 1676 (C^4–C=O), 1641 (C^5–C=O). ^{1}H NMR spectrum, δ, ppm: 7.04–8.15 group of signals (3Ph). Found, %: C 75.55; H 3.94; N 3.69. $C_{24}H_{15}NO_4$. Calculated, %: C 75.58; H 3.96; N 3.67.

4,5-Dibenzoyl-1-(4-methoxyphenyl)-1*H*-pyrrole-2,3-dione (Id). Yield 67%, mp 219–220°C (decomp., benzene). IR spectrum, ν, cm^{-1}: 1770 (C^2=O), 1726 (C^3=O), 1678 (C^4–C=O), 1641 (C^5–C=O). ^{1}H NMR spectrum, δ, ppm: 3.71 s (3H, OMe), 6.94-8.14 group of signals (14H, 2Ph + C$_6$H$_4$). Found, %: C 72.96; H 4.17; N 3.45. $C_{25}H_{17}NO_5$. Calculated, %: C 72.99; H 4.16; N 3.40.

4,5-Di(4-toluoyl)-1-phenyl-1*H*-pyrrole-2,3-dione (Ie). Yield 68%, mp 206–207°C (decomp., benzene). IR spectrum, ν, cm^{-1}: 1775 (C^2=O), 1725 (C^3=O), 1673 (C^4–C=O), 1647 (C^5–C=O). ^{1}H NMR spectrum, δ, ppm: 2.33 s (3H, Me), 2.39 s (3H, Me), 7.18-8.03 group of signals (13H, Ph + 2C$_6$H$_4$). Found, %: C 76.23; H 4.65; N 3.45. $C_{26}H_{19}NO_4$. Calculated, %: C 76.27; H 4.68; N 3.42.

(*Z*)-1,4-Bis(2,5-dimethylphenyl)-2-phenylaminobut-2-ene-1,4-dione (IIIa). A solution of 0.01 mol of bis(2,5-dimethylbenzoyl)acetylene and 0.01 mol of aniline in 30 ml of anhydrous benzene was boiled for 5 min (TLC monitoring), 30 ml of warm petroleum ether (40–70) was added, the solution was cooled, the formed precipitate was filtered off. Yield 91%, mp 101–102°C (benzene–petroleum ether, 1:1). IR spectrum, ν, cm^{-1}: 3150 br. (NH), 1678 (C^1=O), 1600 (C^4=O in intramolecular hydrogen bond). ^{1}H NMR spectrum, δ, ppm: 2.29 s (6H, 2Me), 2.39 s (3H, Me), 2.42 s (3H, Me), 5.78 s (1H, CH), 7.01–7.63 group of signals (11H, Ph + 2C$_6$H$_3$), 12.06 br.s (1H, NH). Found, %: C 81.45; H 6.55; N 3.66. $C_{26}H_{25}NO_2$. Calculated, %: C 81.43; H 6.57; N 3.65.

(*Z*)-1,4-Bis(2,5-dimethylphenyl)-2-(4-methoxyphenylamino)but-2-ene-1,4-dione (IIIb) was similarly obtained. Yield 89%, mp 97–98°C (benzene–petroleum ether, 1:1). IR spectrum, ν, cm^{-1}: 3160 br. (NH), 1665 (C^1=O), 1605 (C^4=O in intramolecular hydrogen bond). ^{1}H NMR spectrum, δ, ppm: 2.29 s (6H, 2Me), 2.36 s (3H, Me), 2.42 s (3H, Me), 3.66 s (3H, OMe), 5.70 s (1H, CH), 6.78–7.61 group of signals (10H, C$_6$H$_4$ + 2C$_6$H$_3$), 12.04 br.s (1H, NH). Found, %: C 78.45; H 6.56; N 3.37. $C_{27}H_{27}NO_3$. Calculated, %: C 78.42; H 6.58; N 3.39.

2,3-Bis(2,5-dimethylbenzoyl)quinolin-4(1*H*)-one (IVa). A solution of 2.5 mmol of compound **Ia** in 2 ml of Dowtherm A was heated at 210°C for 15 min (till the end of CO bubbles liberation), the solution was cooled, diluted with 10 ml of petroleum ether (40–70), the formed precipitate was filtered off. Yield 89%, mp 211–212°C (toluene). IR spectrum, ν, cm^{-1}: 3265 br. (NH), 1668 (C^3–C=O), 1635 (C^2–C=O, C^4=O). ^{1}H NMR spectrum, δ, ppm: 2.16 s (3H, Me), 2.21 s (6H, 2Me), 2.52 s (3H, Me), 7.02–8.11 group of signals (10H, C_6H_4 + 2C_6H_3), 12.79 br.s (1H, NH). Found, %: C 79.22; H 5.64; N 3.46. $C_{27}H_{23}NO_3$. Calculated, %: C 79.20; H 5.66; N 3.42.

Compounds **IVb–IVh** were obtained in a similar way.

2,3-Bis(2,5-dimethylbenzoyl)-6-methoxyquinolin-4(1*H*)-one (IVb). Yield 90%, mp 271-272°C (ethyl acetate). IR spectrum, ν, cm^{-1}: 3250 br. (NH), 1666 (C^3–C=O), 1637 (C^2–C=O, C^4=O). ^{1}H NMR spectrum, δ, ppm: 2.15 s (3H, Me), 2.21 s (6H, 2Me), 2.52 s (3H, Me), 3.85 s (3H, OMe), 7.02–7.72 group of signals (9H, 3C_6H_3), 12.81 br.s (1H, NH). Found, %: C 76.50; H 5.77; N 3.17. $C_{28}H_{25}NO_4$. Calculated, %: C 76.52; H 5.73; N 3.19.

2,3-Dibenzoylquinolin-4(1*H*)-one (IVc). Yield 91%, mp 248-249°C (toluene–acetonitrile, 1:1). IR spectrum, ν, cm^{-1}: 3200 br. (NH), 1682 (C^3–C=O), 1647 (C^2–C=O, C^4=O). ^{1}H NMR spectrum, δ, ppm: 7.41–8.16 group of signals (14H, 2Ph + C_6H_4), 12.85 br.s (1H, NH). Found, %: 78.16; H 4.25; N 3.99. $C_{23}H_{15}NO_3$. СычandСле-НО, %: C 78.18; H 4.28; N 3.96.

2,3-Dibenzoyl-6-methoxyquinolin-4(1*H*)-one (IVd). Yield 89%, mp 256–257°C (ethyl acetate). IR spectrum, ν, cm^{-1}: 3200 br. (NH), 1670 (C^3–C=O, C^2–C=O, C^4=O). ^{1}H NMR spectrum, δ, ppm: 3.88 s (3H, OMe), 7.40–7.90 group of signals (13H, 2Ph + C_6H_3), 12.86 br.s (1H, NH). Found, %: C 75.15; H 4.40; N 3.63. $C_{24}H_{17}NO_4$. Calculated, %: C 75.19; H 4.47; N 3.65.

2,3-Di(4-toluoyl)quinolin-4(1*H*)-one (IVe). Yield 92%, mp 286–287°C (toluene). IR spectrum, ν, cm^{-1}: 3200 br. (NH), 1670 (C^3–C=O), 1645 (C^2–C=O, C^4=O). ^{1}H NMR spectrum, δ, ppm: 2.35 s (6H, 2Me), 7.21–8.15 group of signals (12H, 3C_6H_4), 12.77 br.s (1H, NH). Found, %: 78.76; H 5.05; N 3.63. $C_{25}H_{19}NO_3$. Calculated, %: C 78.72; H 5.02; N 3.67.

REFERENCES

1. Silaichev, P.S., Chudinova, M.A., Slepukhin, P.A., and Maslivets, A.N., *Zh. Org. Khim.,* 2012, vol. 48, p. 114.
2. Kollenz, G., Igel, H., and Ziegler, E., *Monatsh. Chem.,* 1972, vol. 103, p. 450.
3. Briehl, H., Lukosch, A., and Wentrup, C., *J. Org. Chem*., 1984, 15, p. 2772.
4. Maslivets, A.N., Krasnykh, O.P., Cmirnova, L.I., and Andreichikov, Yu.S., *Zh. Org. Khim*., 1989, vol. 75, p. 1045.
5. Lisovenko, N.Yu., Aliev, Z.G., and Maslivets, A.N., *Zh. Org. Khim*., 2010, vol. 46, p. 941.
6. Paradisi, C., Plato, M., Quintily, U., Scorrano, G., and Valle, G., *J. Org. Chem*., 1981, vol. 25, p. 5156.
7. Prakash, O., Batra, A., Chaudhri, V., and Prakash, R., *Tetrahedron, Lett*., 2005, vol. 16, p. 2877.