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Five-Membered 2,3-Dioxoheterocycles: XCV.* Recyclization of 4-Benzoyl-5-phenylfuran-2,3-dione at the Action of Substituted 1,3,3-Trimethyl-2-azaspiro[4.5]dec-1-enes. Crystal and Molecular Structure of Substituted 5-(2-Azaspiro[4.5]dec-1-ylidene)cyclopent-3-ene-1,2-dione

V. V. Konovalova[a], Yu.V. Shklyaev[a], P. A. Slepukhin[b], and A. N. Maslivets[c]

[a]*Institute of Technical Chemistry, Ural Branch of Russian Academy of Sciences, Perm, Russia*
[b]*Postovskii Institute of Organic Synthesis, Ural Branch of Russian Academy of Sciences, Ekaterinburg, Russia*
[c]*Perm State National Research University, Perm, 614990 Russia*
e-mail: koh2@psu.ru

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Abstract—4-Benzoyl-5-phenylfuran-2,3-dione reacts with 2',5',5'-trimethyl-4',5'-dihydro-4*H*-spiro[naphthalene-1,3'-pyrrol]-4-one and 8-(2-methoxy-5-methylphenyl)-1,3,3,9-tetramethyl-2-azaspiro[4.5]deca-1,7-dien-6-one with the formation of (Z)-3-benzoyl-5-(5',5'-dimethyl-4-oxo-4*H*-spiro[naphthalene-1,3'-pyrrolidin]-2'-ylidene)-4-phenylcyclopent-3-ene-1,2-dione, whose structure was proved by XRD analysis, and of (Z)-3-benzoyl-5-{8-(2-methoxy-5-methylphenyl)-3,3,9-trimethyl-6-oxo-2-azaspiro[4.5]dec-7-en-1-ylidene}-4-phenylcyclopent-3-ene-1,2-dione.

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5-Arylfuran-2,3-diones at heating suffer a thermal decarbonylation providing aroylketenes, which are involved in intermolecular reactions of cycloaddition with active dienophiles [2, 3] and acylate weak nucleophiles giving aroylacetyl derivatives [2, 4]. At the same time the proper furandiones are capable of acylating nucleophilic reagents at a temperature that is lower than the temperature required for aroylketenes generation leading to the formation of aroylpyruvoyl derivatives [2, 5]. We described formerly the reaction between 5-arylfuran-2,3-diones and 1,3,3-trimethyl-2-azaspiro[4.5]dec-1-ene (2',5',5'-trimethyl-4',5'-dihydro-4*H*-spiro[naphthalene-1,3'-pyrrol]-4-one) affording the products of β-CH-acylation with the furandiones of the tautomeric enamino form of the spiropyrrolone, (2*Z*,5*Z*)-1-aryl-3-hydroxy-5-(5',5'-dimethyl-4-oxo-2'*H*,4*H*-spiro[naphthalene-1,3'-pyrrolidin]-2'-ylidene) pent-2-ene-1,4-diones [6]. In extension of these studies we attempted to modify the structure of furan-2,3-diones aiming at changing the regiodirection of their reaction with substituted 1,3,3-trimethyl-2-azaspiro[4.5]dec-1-enes.

The reaction of 4-benzoyl-5-phenylfuran-2,3-dione (**I**) with 2',5',5'-trimethyl-4',5'-dihydro-4*H*-spiro[naphthalene-1,3'-pyrrol]-4-one (**IIa**) and 8-(2-methoxy-5-methylphenyl)-1,3,3,9-tetramethyl-2-azaspiro[4.5]deca-1,7-dien-6-one (**IIb**) in the ratio 1 : 1 at boiling in anhydrous benzene for 30–60 min (till the disappearance of the bright yellow color of the initial furandione) afforded in good yield 5-substituted (*Z*)-3-benzoyl-4-phenylcyclopent-3-ene-1,2-diones **IIIa, IIIb**. The structure of compound **IIIa** was confirmed by XRD analysis.

Compound **IIIa** is dark red, compound **IIIb** is dark violet crystalline substances, they are readily soluble in DMSO and DMF, sparingly soluble in alcohols and

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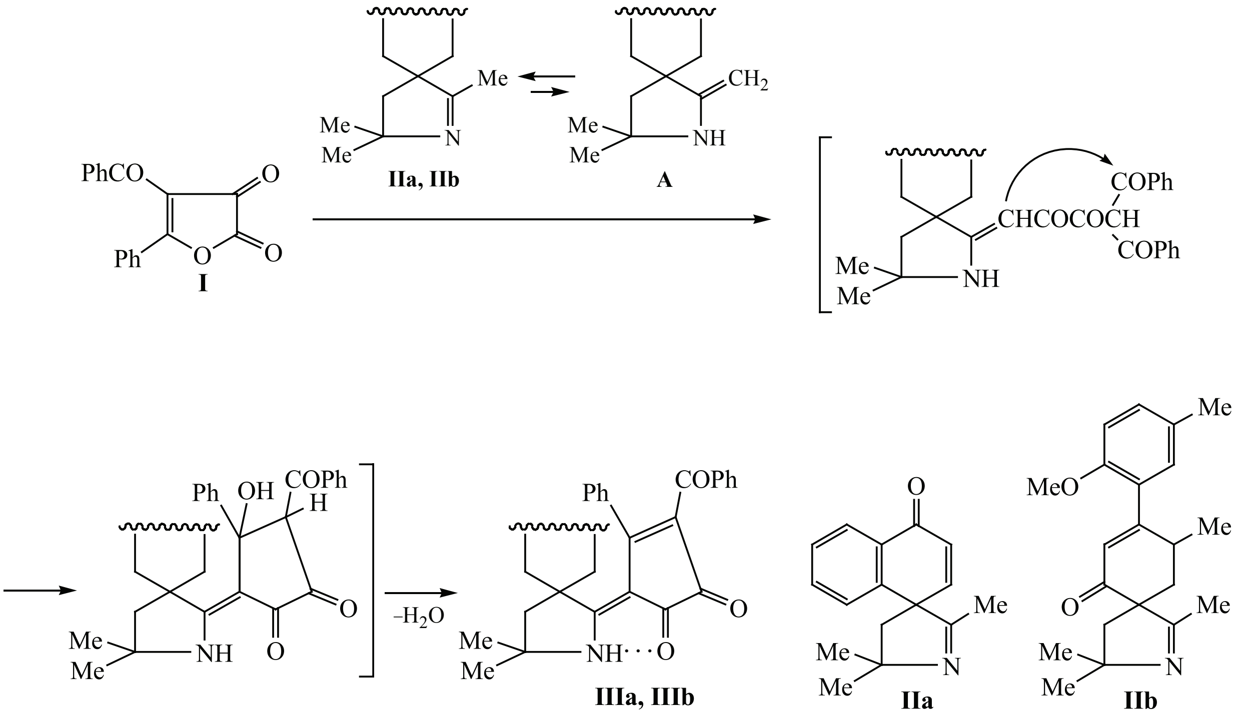
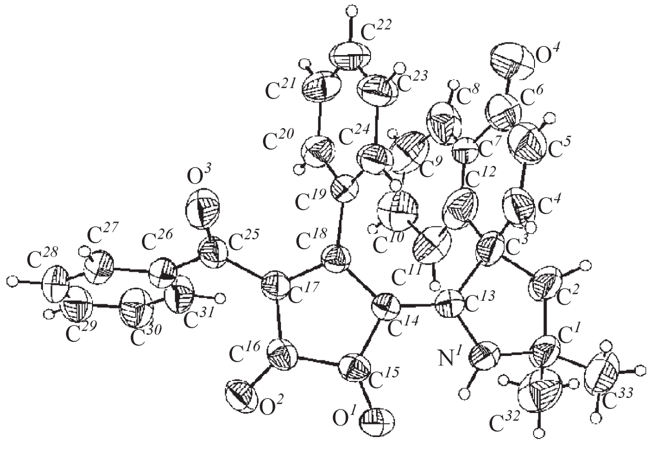
*For communication XCIV, see [1].



haloalkanes, insoluble in water and alkanes.

The IR spectra of compounds **IIIa, IIIb** contain the bands of stretching vibrations of NH group involved into the formation of intramolecular hydrogen bond (HB) as a broad band at 3263–3265 cm^{-1}, of the keto carbonyl group C^2=O as a broad band at 1689–1692 cm^{-1}, of the keto carbonyl group PhC=O and the keto carbonyl group of the naphthalene or cyclohexadiene fragment as a broad band at 1655–1661 cm^{-1}, and the keto carbonyl group C^1=O involved in the formation of the intramolecular hydrogen bond at 1611–1614 cm^{-1}.



General view of the molecule of (*Z*)-3-benzoyl-5-(5',5'-dimethyl-4-oxo-4*H*-spiro[naphthalene-1,3'-pyrrolidin]-2'-ylidene)-4-phenylcyclopent-3-ene-1,2-dione (**IIIa**) according to XRD data..

In the ^{1}H NMR spectra of compounds **IIIa, IIIb** alongside with the proton signals of the aromatic rings and the groups attached thereto two singlets are present from the protons of the two methyl groups of the pyrrolidine fragment in the region 1.15–1.50 and 1.19–1.53 ppm, a doublet of doublets from the CH_2 group of the pyrrolidine fragment (1.94–2.27 ppm), and a singlet of the proton of the NH group at 10.74–10.81 ppm.

According to the XRD data (see the figure) the dark red crystals of compound **IIIa** crystallize in the centrosymmetrical space group P-1 of the triclinic crystal system. The unit cell is formed by two crystallographically independent molecules of similar geometry. The bond lengths and bond angles of the molecules possess close values approaching the standards. The bond lengths in the conjugated system of C–C bond of the dioxocyclopentene fragment (the bond lengths with substituents included) are to a large extent leveled (1.37–1.49 Å). At the same time the length of the C^{15}–C^{16} bond between two keto groups is 1.55 Å, the value close to the standard length of the ordinary C–C bond, indicating the absence of the conjugation of the π-electron density between these moieties. The pyrrole fragment is nonplanar. Its orientation with respect to the dioxocyclopentene fragment is governed by the intramolecular hydrogen bond NH···O.

Apparently in the course of the reaction under consideration the β-CH group of the tautomeric enamino form **A** of the substituted 1,3,3-trimethyl-2-azaspiro[4.5]dec-1-enes **IIa, IIb** undergoes the acylation by the carbonyl group in the position *2* of 4-benzoyl-5-phenylfuran-2,3-dione (**I**), the furandione ring opens at the O^{1}–C^{2} bond and the successive intramolecular cyclization occurs with water elimination. The reaction presented is an example of building up a stereoregular ensemble from two polyfunctional systems based on a direct recyclization of 4-benzoyl-5-phenylfuran-2,3-dione under the action of substituted 1-methyl-2-azaspiro[4.5]dec-1-enes.

The introduction of an additional benzoyl group into the position *4* of the furandione ring led to the change in the previously described reactions.

EXPERIMENTAL

IR spectra of compounds obtained were recorded on an IR Fourier spectrophotometer IFS 66 (Bruker) in mineral oil. ^{1}H and ^{13}C NMR spectra were registered on a spectrometer Mercury-300BB (300 MHz) in $CDCl_3$, internal reference HMDS. The homogeneity of compounds synthesized was confirmed by TLC on Sorbfil plates, eluents ethyl acetate–benzene, 1 : 5, ethyl acetate; spots visualized with 0.5% chloranil solution in toluene.

(*Z*)-3-Benzoyl-5-(5',5'-dimethyl-4-oxo-4*H*-spiro[naphthalene-1,3'-pyrrolidin]-2'-ylidene)-4-phenylcyclopent-3-ene-1,2-dione (IIIa). A solution of 1.0 mmol of 4-benzoyl-5-phenylfuran-2,3-dione (**I**) and 1.0 mmol of reagent **IIa** in 30 ml of anhydrous benzene was boiled for 60 min, cooled, the separated precipitate was filtered off. Yield 89%, mp 218–219°C (decomp., ethyl acetate). IR spectrum, cm^{-1}: 3263 br (NH in HB), 1689 (C^{2}=O), 1655 br (PhC=O, CO_{naphth}), 1611 (C^{1}=O in HB). ^{1}H NMR spectrum, δ, ppm: 1.50 s, 1.53 s (6H, 2Me), 2.21, 2.27 d.d (2H, CH_2, *J* 13.8 Hz), 5.88 d ($1H_{naphth}$), 6.89 d ($1H_{naphth}$), 6.95–7.81 group of signals (14H, 2Ph, C_6H_4), 10.74 s (1H, NH). Found, %: C 79.19; H 5.16; N 2.61. $C_{33}H_{25}NO_4$. Calculated, %: C 79.34; H 5.04; N 2.80.

XRD analysis of compound IIIa was carried out using a fragment of a prismatic crystal of the size 0.25 × 0.20 × 0.15 mm on a single-crystal automatic diffractometer Xcalibur 3 with a CCD-detector by a standard procedure (MoK_α-radiation, 295(2) K, ω-scanning, step of scanning 1є) [7]. The correction for extinction was not introduced due to its negligible value (μ 0.086 mm^{-1}). Within the scattering angles $2.66 < \theta < 28.28°$ 24707 reflections were collected, 11991 among them independent (R_{int} 0.0255), 5591 reflections with $I > 2\sigma(I)$. Crystal system triclinic, *a* 9.8236(8), *b* 14.7005(10), *c* 18.8767(13) Å, α 101.190(6), β 98.939(6), γ 104.011(7) deg, space group P-1. Completeness for $\theta < 26.00°$ 97.1%. The structure was solved by the direct method and refined with the use of software SHELXTL [8] with respect to F^2 in the anisotropic approximation for the nonhydrogen atoms (the hydrogen atoms were introduced into the refinement in the rider model in the isotropic approximation with dependent thermal parameters). The final refinement parameters are as follows: R_1 0.0553, wR_2 0.1475 [for reflections with $I > 2\sigma(I)$], R_1 0.1204, wR_2 0.1630 (for all reflections) for *Z* 4, *GOOF* 1.015. The peaks of the residual electron density 1.063 and –0.316 ēÅ^{-3}.

(*Z*)-3-Benzoyl-5-{3,3,9-trimethyl-8-(5-methyl-2-methoxyphenyl)-6-oxo-2-azaspiro[4.5]dec-7-ene-1-ylidene}-4-phenylcyclopent-3-ene-1,2-dione (IIIb) was analogously obtained. Yield 92%, mp 207–209°C (decomp., ethyl acetate). IR spectrum, cm^{-1}: 3265 br (NH in HB), 1692 (C^{2}=O), 1661 br (PhC=O, $CO_{cyclohex}$), 1614 (C^{1}=O in HB). ^{1}H NMR spectrum, δ, ppm: 0.93 d (3H, 9-Me), 1.15 s, 1.19 s (6H, 2Me), 1.94, 1.98 d.d (2H, $C^{4}H_2$, *J* 5.1 Hz), 2.10 t (2H, $C^{10}H_2$, *J* 13.4 Hz), 2.30 s (3H, 5-Me), 3.32 br.s (1H, H^{9}), 3.80 s (3H, OMe), 6.13 s (1H, H^{7}), 6.75–7.74 group of signals (13H, 2Ph + C_6H_3), 10.81s (1H, NH). Found, %: C 77.87; H 6.02; N 2.22. $C_{38}H_{35}NO_5$. Calculated, %: C 77.93; H 6.02; N 2.39.

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