

SHORT
COMMUNICATIONSMild Acylation of Fischer Indole
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Received July 4, 2008

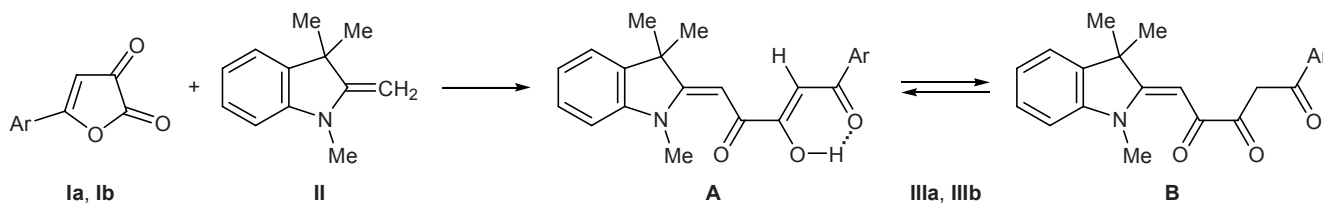
DOI: 10.1134/S107042800906027X

Reactions of 2,3-dihydrofuran-2,3-diones with secondary heterocyclic enamines were not studied previously. We examined reactions of 5-aryl-2,3-furan-2,3-diones **Ia** and **Ib** with 1,3,3-trimethyl-2-methylidene-2,3-dihydro-1*H*-indole (**II**, Fischer indole) at a molar ratio of 1:1 on heating in boiling anhydrous benzene (reaction time 1–2 min, until bright yellow color typical of initial furandiones **I** disappeared) and obtained in good yields (2*Z*)-1-aryl-3-hydroxy-5-(1,3,3-trimethyl-2,3-dihydro-1*H*-indol-2-ylidene)pent-2-ene-1,4-diones **IIIa** and **IIIb**. The spectral parameters of compounds **IIIa** and **IIIb** indicated that they exist in DMSO-*d*₆ solution as mixtures of enol and diketone tautomers **A** and **B** at a ratio of ~5:1. Their spectra were similar to those of model (2*Z*,5*Z*)-3-hydroxy-5-{8,8-dimethyl-2,3,8,9-tetrahydro[1,4]dioxino[2,3-*g*]-isoquinolin-6(7*H*)-ylidene}-1-phenylpent-2-ene-1,4-dione whose structure was confirmed by the X-ray diffraction data.

Presumably, the described transformation involves acylation of the exocyclic methylene group in indole **II** by the carbonyl group in position 2 of 5-aryl-2,3-dihydrofuran-2,3-dione **Ia** or **Ib**, followed by opening of the furan ring at the O¹–C² bond, as was reported for the reaction of 5-aryl-2,3-dihydrofuran-2,3-diones with 1-methyl-3,4-dihydroisoquinolines [1, 2].

(2*Z*)-3-Hydroxy-5-(1,3,3-trimethyl-2,3-dihydro-1*H*-indol-2-ylidene)-1-phenylpent-2-ene-1,4-dione (**IIIa**). A solution of 3.0 mmol of 5-phenyl-2,3-dihydrofuran-2,3-dione (**Ia**) and 3.0 mmol of Fischer indole **II** in 20 ml of anhydrous benzene was heated for 1 min under reflux. The mixture was cooled, and the precipitate was filtered off. Yield 89%, mp 157–159°C (decomp.; from ethanol). IR spectrum, ν , cm⁻¹: 3170 br (OH, assoc.), 1608 br (C=O, assoc.). ¹H NMR spectrum, δ , ppm: **A**: 1.74 s (6H, Me), 3.38 s (3H, Me), 6.18 s (1H, 5-H), 7.13 s (1H, 2-H), 7.08–8.09 m (9H, H_{arom}), 16.08 br.s (1H, OH); **B**: 1.65 s (6H, Me), 3.35 s (3H, Me), 4.48 s (2H, 2-H), 5.96 s (1H, 5-H), 7.06–7.99 m (9H, H_{arom}). Found, %: C 75.91; H 6.21; N 3.84. C₂₂H₂₁NO₃. Calculated, %: C 76.06; H 6.09; N 4.03.

(2*Z*)-3-Hydroxy-1-(4-methylphenyl)-5-(1,3,3-trimethyl-2,3-dihydro-1*H*-indol-2-ylidene)pent-2-ene-1,4-dione (**IIIb**) was synthesized in a similar way. Yield 87%, mp 170–172°C (decomp.; from ethanol). IR spectrum, ν , cm⁻¹: 3160 br (OH, assoc.), 1608 br (C=O, assoc.). ¹H NMR spectrum, δ , ppm: **A**: 1.74 s (6H, Me), 2.41 s (3H, MeC₆H₄), 3.37 s (3H, Me), 6.18 s (1H, 5-H), 7.09 s (1H, 2-H), 7.08–7.98 m (8H, H_{arom}), 16.15 br.s (1H, OH); **B**: 1.65 s (6H, Me), 2.39 s (3H, MeC₆H₄), 3.34 s (3H, Me), 4.45 s (2H, 2-H),

Ar = Ph (**a**), 4-MeC₆H₄ (**b**).

5.96 s (1H, 5-H), 7.06–7.89 m (8H, H_{arom}). Found, %: C 76.42; H 6.61; N 3.70. C₂₃H₂₃NO₃. Calculated, %: C 76.43; H 6.41; N 3.88.

The IR spectra were recorded on an FMS-1201 spectrometer from samples dispersed in mineral oil. The ¹H NMR spectra were measured on a Bruker WP-400 instrument from solutions in DMSO-*d*₆ using tetramethylsilane as internal reference. The purity of the products was checked by TLC on Silufol plates using ethyl acetate–benzene (1:5) as eluent; development with iodine vapor.

This study was performed under financial support by the Russian Foundation for Basic Research (project nos. 08-03-01032, 07-03-96036).

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