ISSN 1070-4280, Russian Journal of Organic Chemistry, 2011, Vol. 47, No. 7, pp. 1119–1120. © Pleiades Publishing, Ltd., 2011.
Original Russian Text © V.V. Konovalova, Yu.V. Shklyaev, A.N. Maslivets, 2011, published in Zhurnal Organicheskoi Khimii, 2011, Vol. 47, No. 7, pp. 1099–1100.

SHORT COMMUNICATIONS

Acylation of 2′,5′,5′-Trimethyl-4′,5′-dihydro-4*H*-spiro-[naphthalene-1,3′-pyrrol]-4-one with 5-Arylfuran-2,3-diones

V. V. Konovalova[a], **Yu. V. Shklyaev**[a], **and A. N. Maslivets**[b]

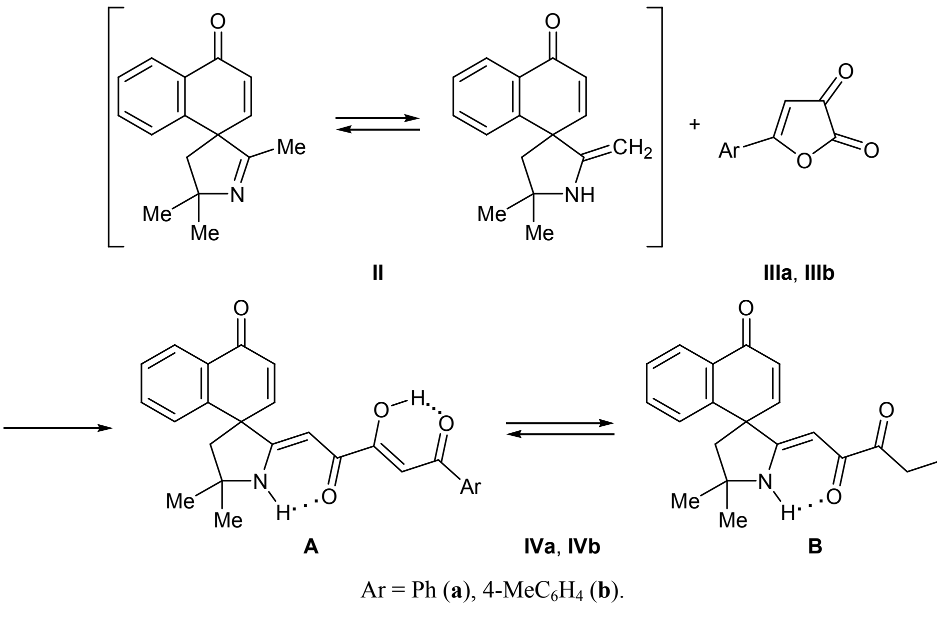
[a] *Institute of Technical Chemistry, Ural Division, Russian Academy of Sciences, Perm, Russia*
[b] *Perm State University, ul. Bukireva 15, Perm, 614990 Russia*
e-mail: koh2@psu.ru

Received October 16, 2010

DOI: 10.1134/S1070428011070256

We previously showed that cyclic Schiff bases, e.g., 3,3-dialkyl-1-methyl-3,4-dihydroisoquinolines (**I**), readily react with unsaturated electrophiles such as isocyanates [1], hexafluoroisopropylidenemalononitrile [2], 3-nitro-2-trifluoromethylchromene [3], and 5-arylfuran-2,3-diones [4]. Although enamino tautomer of compounds **I** was not detected by modern instrumental methods, the above reactions unambiguously indicated formation of that tautomer as reactive species at least in solution. Spirocyclic 2-methyl-4,5-dihydro-1*H*-pyrroles, in particular 2′,5′,5′-trimethyl-4′,5′-dihydro-4*H*-spiro[naphthalene-1,3′-pyrrol]-4-one (**II**), also exist in the imino form [5]; enamino tautomer is possible for derivatives containing an electron-acceptor substituent on the β-carbon atom in the enamine fragment. Taking into account structural similarity of compounds **I** and **II**, we presumed that the latter are also capable of reacting with 5-arylfuran-2,3-diones, though in this case steric hindrances should be more considerable than for isoquinoline derivatives **I**.

In fact, 2′,5′,5′-trimethyl-4′,5′-dihydro-4*H*-spiro-[naphthalene-1,3′-pyrrol]-4-one (**II**) reacted with an equimolar amount of 5-arylfuran-2,3-dione **IIIa** or **IIIb** on heating in anhydrous benzene over a period of 3–4 h (TLC monitoring) to give the corresponding (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 **IVa** and **IVb**. The spectral parameters of compounds **IVa** and **IVb** indicated that they exist in DMSO-d_6 as mixtures of keto enol and



Ar = Ph (**a**), 4-MeC_6H_4 (**b**).

diketone tautomers **A** and **B** at a ratio of ~5:1. Presumably, the described reaction involves acylation of the $=CH_2$ carbon atom in the enamino tautomer of **II** by the $C^2=O$ carbonyl group in furandione **III**, followed by opening of the furan ring at the $O^1–C^2$ bond, as in the reaction of 5-arylfuran-2,3-diones with 1-methyl-3,4-dihydroisoquinolines [4].

Thus we can state that spirocyclic dihydropyrrole derivatives like **II** also give rise to imine–enamine tautomerism and that considerable steric hindrances created by geminal methyl groups on C^5 and spiro-fused naphthalene fragment on C^3 do not hamper reaction of **II** with 5-arylfuran-2,3-diones.

(2*Z*,5*Z*)-3-Hydroxy-5-(5′,5′-dimethyl-4-oxo-2′*H*,4*H*-spiro[naphthalene-1,3′-pyrrolidin]-2′-ylidene)-1-phenylpent-2-ene-1,4-dione (IVa). A solution of 1.0 mmol of 5-phenylfuran-2,3-dione (**IIIa**) and 1.0 mmol of compound **II** in 20 ml of anhydrous benzene was heated for 4 h under reflux. The mixture was cooled, and the precipitate was filtered off. Yield 82%, mp 194–195°C (decomp., from ethanol). IR spectrum, ν, cm^{-1}: 3150 br (OH, NH), 1660 ($C^4=O$), 1595 br (C=O). ^1H NMR spectrum, δ, ppm: **A**: 1.59 s and 1.65 s (3H each, Me), 2.46 m (2H, 4′-H, *AB* system), 5.08 s (1H, 5″-H), 6.45 d (1H, 3-H), 6.92 s (1H, 2″-H), 7.26 d (1H, 2-H), 7.41–8.06 m (9H, H_{arom}), 10.77 s (1H, NH), 16.04 br.s (1H, OH); **B**: 1.53 s and 1.60 s (3H each, Me), 2.41 m (2H, 4′-H, *AB* system), 4.31 s (2H, 2″-H), 4.85 s (1H, 5″-H), 6.43 d (1H, 3-H), 7.22 d (1H, 2-H), 7.37–8.05 m (9H, H_{arom}), 10.57 s (1H, NH). Found, %: C 75.46; H 5.63; N 3.24. $C_{26}H_{23}NO_4$. Calculated, %: C 75.53; H 5.61; N 3.39.

(2*Z*,5*Z*)-3-Hydroxy-5-(5′,5′-dimethyl-4-oxo-2′*H*,4*H*-spiro[naphthalene-1,3′-pyrrolidin]-2′-ylidene)-1-(4-methylphenyl)pent-2-ene-1,4-dione (IVb) was synthesized in a similar way. Yield 79%, mp 183–185°C (decomp., from ethanol). IR spectrum, ν, cm^{-1}: 3180 br (OH, NH), 1660 ($C^4=O$), 1598 br (C=O). ^1H NMR spectrum, δ, ppm: **A**: 1.59 s and 1.64 s (3H each, Me), 2.41 s (3H, **Me**C_6H_4), 2.45 m (2H, 4′-H, *AB* system), 5.06 s (1H, 5″-H), 6.44 d (1H, 3-H), 6.90 s (1H, 2″-H), 7.25 d (1H, 2-H), 7.49–8.04 m (8H, H_{arom}), 10.82 s (1H, NH), 16.10 br.s (1H, OH); **B**: 1.53 s and 1.58 s (3H each, Me), 2.39 s (3H, **Me**C_6H_4), 2.41 m (2H, 4′-H, *AB* system), 4.33 s (2H, 2″-H), 4.84 s (1H, 5″-H), 6.40 d (1H, 3-H), 7.21 d (1H, 2-H), 7.43–8.00 m (8H, H_{arom}), 10.52 s (1H, NH). Found, %: C 75.69; H 5.95; N 3.17. $C_{27}H_{25}NO_4$. Calculated, %: C 75.86; H 5.89; N 3.28.

The IR spectra were recorded on a UR-20 spectrometer from samples dispersed in mineral oil. The ^1H NMR spectra were measured on a Varian Mercury Plus 300 spectrometer (300 MHz) from solutions in DMSO-d_6 using tetramethylsilane as internal reference. The purity of the isolated compounds was checked by TLC on Silufol plates using ethyl acetate as eluent; spots were developed by treatment with a 0.5% solution of tetrachloro-1,4-benzophenone in toluene.

This study was performed under financial support by the Presidium of the Russian Academy of Sciences (program no. 18), by the Russian Foundation for Basic Research (project no. 08-03-01032), and by the Ural Division of the Russian Academy of Sciences (Scientific Special-Purpose Program "Competition of Scientific Projects of Young Scientists and Post-Graduate Students").

REFERENCES

1. Boronenkova, E.S., Syropyatov, B.Ya., Gorbunov, A.A., Shklyaev, V.S., and Shklyaev, Yu.V., *Khim.-Farm. Zh.*, 1994, vol. 28, no. 8, p. 18.
2. Tyutin, V.Yu., Chkanikov, N.D., Shklyaev, Yu.V., Shklyaev, V.S., Kolomiets, A.F., and Fokin, A.V., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 1992, p. 1888.
3. Korotaev, V.Yu., Sosnovskikh, V.Ya., Kutyashev, I.V., Barkov, A.Yu., and Shklyaev, Yu.V., *Tetrahedron Lett.*, 2008, vol. 49, p. 5376.
4. Khalturina, V.V., Shklyaev, Yu.V., Aliev, Z.G., and Maslivets, A.N., *Russ. J. Org. Chem.*, 2009, vol. 45, p. 728.
5. Nifontov, Yu.V., Glushkov, V.A., and Shklyaev, Yu.V., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 2003, p. 418.