ISSN 1070-4280 Russian Journal of Organic Chemistry, 2006, Vol. 42, No. 5, pp. 778–779. © Pleiades Publishing, Inc. 2006.
Original Russian Text © V.V. Shchepin, P.S. Silaichev, M.I. Kodess, 2006, published in Zhurnal Organicheskoi Khimii, 2006, Vol. 42, No. 5, pp. 793–794.

SHORT
COMMUNICATIONS

# Unexpected Formation of 5'-Aryl-1'-benzyl-4'-methyl-3,4,2',3'-tetrahydro-2,2'-dioxospiro[chroman3,3'-pyrrol]-4-yl Acetates at Acylation of 1-Aryl-2-benzyl-1-hydroxy-9c-methyl-1,2,9b,9c-tetrahydro-5-oxa-2-azacyclopenta[2,3]cyclopropa[1,2-*a*]naphthalene-3,4-diones with Acetic Anhydride

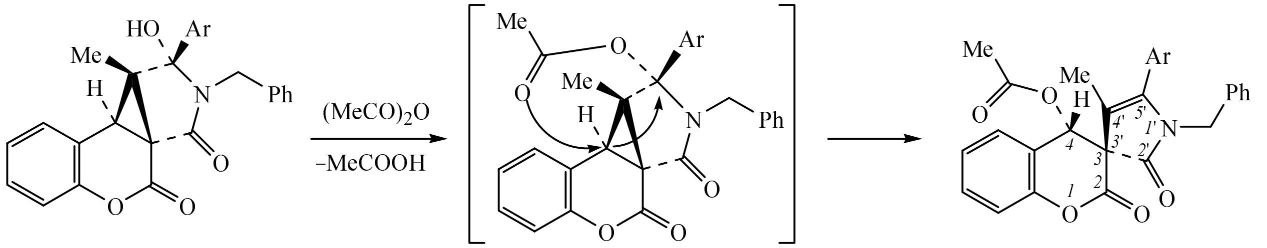
**V.V. Shchepin[a], P.S. Silaichev[a], and M.I. Kodess[b]**

[a]*Perm State University, Perm, 614990 Russia*
[b]*Postovskii Institute of Organic Synthesis, Ural Division, Russian Academy of Sciences, Yekaterinburg, Russia*

Received May 4, 2005

**DOI:** 10.1134/S1070428006050265

In the study of reactions of bromine derivatives of zinc enolates originating from 1-aryl-2,2-dibromoalkanones and zinc with a 6-bromo-2-oxochromen-3-carboxylic acid *N*-benzylamide we obtained 9c-alkyl-1-aryl-2-benzyl-8-bromo-1,2,9b,9c-tetrahydro-1-hydroxy-5-oxa-2-azacyclopenta[2,3]cyclopropa[1,2-*a*]naphthalene-3,4-diones [1]. Here we report on the study of the reactivity in acylation with acetic anhydride of 1-aryl-2-benzyl-9c-methyl-1,2,9b,9c-tetrahydro-1-hydroxy-5-oxa-2-azacyclopenta-[2,3]cyclopropa-[1,2-*a*]naphthalene-3,4-diones **Ia–Ic**. The reaction occurred with a transfer of the reaction site and resulted in formation of spiro compounds: 5'-aryl-1'-benzyl-4'-methyl-3,4,2',3'-tetrahydro-2,2'-dioxospiro-[chroman-3,3'-pyrrol]-4-yl acetates **IIIa–IIIc**.



**Ia–Ic** **IIa–IIc** **IIIa–IIIc**

Ar = 4-$FC_6H_4$ (**a**), 4-$ClC_6H_4$ (**b**), 4-$BrC_6H_4$ (**c**).

The reaction apparently started with acylation of the hydroxy group of substrates **Ia–Ic** to form intermediates **IIa–IIc** which under the reaction conditions undergo rearrangement with the opening of the three-membered ring and acyl group transfer to the atom $C^4$ of the chroman ring affording compounds **IIIa–IIIc**. The composition and structure of compounds **IIIa–IIIc** are proved by elemental analysis, IR, $^1H$ and $^{13}C$ NMR spectroscopy. In the IR spectra appear the characteristic absorption bands of the lactam carbonyl (1710 cm$^{-1}$) and carbonyl groups from the ester and the lacton fragments (1755–1760 cm$^{-1}$). In the $^1H$ NMR spectra characteristic singlet signals are observed in the regions 1.43–1.44, 1.99–2.02, and 6.40–6.43 ppm belonging to the protons of methyl groups and to the proton in position *4* of the chroman ring respectively, and also appears an *AB*-system of the nonequivalent protons of the methylene group from the benzyl substituent in the region 4.22–4.51 ppm with the geminal coupling constant $^2J$ equal 15.5 Hz. The single set of signals in the $^1$H NMR spectra evidences the formation of reaction products as an only geometrical isomer.

In order to confirm the structure of compounds **IIIa–IIIc** obtained we investigated the $^1$H and $^{13}$C NMR spectra of compound **IIIb**, registering the $^{13}$C NMR spectra both with and without decoupling from protons for measuring the coupling constants $^nJ_{C,H}$. The proton and carbon signals were assigned using 2D experiments NOESY and HSQC. NOESY spectra were also applied to establishing the configuration of compound **IIIb**.

The analysis of the spectra made it possible to establish the mutual spatial arrangement of the pyrrole spirocycle and the pyran ring. These conclusions were based on the dependence of the vicinal coupling constants $^{13}$C–$^1$H ($^3J_{C,H}$) between proton $H^4$ and atoms $C^{2'}$, $C^{4'}$ on the value of the dihedral angle θ. The corresponding constants were unambiguously estimated from the $^{13}$C NMR spectrum without decoupling from protons. In the spectrum of compound **IIIb** the signal of the carbonyl atom $C^{2'}$ appears as a doublet of triplets, that of atom $C^4$, as quartet of doublets, where the splitting into the doublet is due to the coupling with proton $H^4$: $^3J_{C^{2'},H^4}$ 5.2, $^3J_{C^{4'},H^4}$ 2.4 Hz.

Taking into consideration the most probable conformation of the six-membered ring the established values of the coupling constants suggest that proton $H^4$ and atom $C^{2'}$ occupy pseudoaxial positions, i.e., in the *trans*-position to each other, and atoms $H^4$ and $C^{4'}$ are located in the *cis*-position. This conclusion was confirmed by the spectra 2D NOESY containing a cross-peak between proton $H^4$ and the methyl group attached to $C^{4'}$ showing their close spatial position.

**5'-Aryl-1'-benzyl-4'-methyl-3,4,2',3'-tetrahydro-2,2'-dioxospiro[chroman-3,3'-pyrrol]-4-yl acetate (IIIa–IIIc)**. In excess acetic anhydride with tree drops of tribytylamine added 0.005 mol of compound **Ia–Ic** was boiled for 3 h, then the arising acetic acid and excess acetic anhydride was distilled off. The residue was dissolved in boiling benzene and precipitated with petroleum ether. The reaction product was recrystallized from ethyl acetate.

**1'-Benzyl-4'-methyl-3,4,2',3'-tetrahydro-2,2'-dioxo-5'-(4-fluorophenyl)spiro[chroman-3,3'-pyrrol]-4-yl acetate (IIIa).** Yield 51%, mp 142–144°C. IR spectrum, ν, cm$^{-1}$: 1710, 1760. $^1$H NMR spectrum, δ, ppm: 1.44 s (3H, Me), 2.02 s (3H, $\underline{\text{Me}}$COO), 4.23 d, 4.51 d (2H, $\underline{\text{CH}_2}$Ph, $^2J$ 15.5 Hz), 6.43 s (1H, $H^4$), 6.65–7.25 m (13H, $C_6H_4$, $C_6H_5$, 4-$FC_6H_4$). Found, %: C 71.18; H 4.59; N 2.85. $C_{28}H_{22}FNO_5$. Calculated, %: C 71.33; H 4.70; N 2.97

**1'-Benzyl-4'-methyl-3,4,2',3'-tetrahydro-2,2'-dioxo-5'-(4-chlorophenyl)spiro[chroman-3,3'-pyrrol]-4-ylacetate (IIIb).** Yield 57%, mp 177–178°C. IR spectrum, ν, cm$^{-1}$: 1710, 1755. $^1$H NMR spectrum (400 MHz), δ, ppm: 1.53 s (3H, Me), 2.09 s (3H, $\underline{\text{Me}}$COO), 4.36 d, 4.62 d (2H, $\underline{\text{CH}_2}$Ph, $^2J$ 15.5 Hz), 6.56 s (1H, $H^4$), 6.88 m ($2H_m$, Ph), 6.94 d ($2H_m$, 4-$ClC_6H_4$, $J$ 8.5 Hz), 7.17 m (4H), 7.21–7.27 m (2H), 7.30 d ($2H_O$, 4-$ClC_6H_4$, $J$ 8.5 Hz), 7.42 d.d.d (1H, $H^6$, $J$ 8.3, 6.5, 2.3 Hz); (100 MHz): 1.44 s (3H, Me), 2.01 s (3H, $\underline{\text{Me}}$COO), 4.23 d, 4.51 d (2H, $\underline{\text{CH}_2}$Ph, $^2J$ 15.5 Hz), 6.41 s (1H, $C^4H$), 6.70–7.30 m (13H, $C_6H_4$, $C_6H_5$, 4-$ClC_6H_4$). $^{13}$C NMR spectrum, δ, ppm: 9.88 (Me), 20.48 ($\underline{\text{Me}}$CO), 44.63 ($NCH_2$), 61.10 ($C^3$), 67.80 ($C^4$), 111.77 ($C^{4'}$), 116.58 ($C^8$), 119.42 ($C^{4a}$), 125.14 ($C^6$), 126.64 ($C^5$), 127.32 ($C^o$, Ph), 127.35 ($C^i$, 4-$ClC_6H_4$), 127.39 ($C^n$, Ph), 128.40 ($C^m$, Ph), 128.78 ($C^m$, 4-$ClC_6H_4$), 130.64 ($C^7$), 130.87 ($C^o$, 4-$ClC_6H_4$), 135.46 ($C^n$, 4-$ClC_6H_4$), 136.40 ($C^i$, Ph), 141.65 ($C^{5'}$), 150.49 ($C^{8a}$), 162.09 ($C^2$), 169.57 (COO), 170.65 ($C^{2'}$). Found, %: C68.80; H 4.40; N 2.74. $C_{28}H_{22}ClNO_5$. Calculated, %: C 68.92; H 4.54; N 2.87.

**1'-Benzyl-4'-methyl-3,4,2',3'-tetrahydro-2,2'-dioxo-5'-(4-bromophenyl)spiro[chroman-3,3'-pyrrol]-4-ylacetate (IIIb).** Yield 59%, mp 165–166°C. IR spectrum, cm$^{-1}$: 1710, 1755. $^1$H NMR spectrum, δ, ppm: 1.43 s (3H, Me), 1.99 s (3H, $\underline{\text{Me}}$COO), 4.22 d, 4.50 d (2H, $\underline{\text{CH}_2}$Ph, $^2J$ 15.5), 6.40 s (1H, $H^4$), 6.65–7.40 m (13H, $C_6H_4$, $C_6H_5$, 4-$BrC_6H_4$). Found, %: C63.01; H 4.07; N 2.49. $C_{28}H_{22}BrNO_5$. Calculated, %: C 63.17; H 4.16; N 2.63

IR spectra were recorded on a spectrometer UR-20 from mulls of individual compounds in mineral oil. $^1$H NMR spectra of compounds **IIIa–IIIc** dissolved in $CDCl_3$ were registered on a spectrometer Tesla BS-576A (100 MHz), internal reference HMDS. NMR spectra of compound **IIIb** were registered from solution in $CDCl_3$ on a spectrometer Bruker DRX-400 ( at 400 MHz for $^1$H and 100 MHz for $^{13}$C), internal reference TMS.

The study was carried out under financial support of the Russian Foundation for Basic Research (grants nos. 04-03-96036, 04-03-97505) and of the Federal Agency of Education (grant no. A.04-2.11-492).

## REFERENCES

1. Shchepin, V.V., Silaichev, P.S., Shchepin, R.V., Ezhikova, M.A., and Kodess, M.I., *Zh. Org. Khim.,* 2005, vol. 41, p. 539.