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UNEXPECTED SYNTHESIS OF SUBSTITUTED 9b,9c-DIHYDRO-5-OXA-2-AZACYCLOPENTA[2,3]-CYCLOPROPA[1,2-*a*]NAPHTHALENE-1,3,4-TRIONES ACCORDING TO A MODIFIED REFORMATSKY REACTION

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We showed earlier that derivatives of 2-oxochromene-3-carboxylic acid are cyclopropanated by bromine-containing zinc enolates, obtained from 1-aryl-2,2-dibromoalkanones and zinc, to form cyclopropane derivatives containing an aroyl group on the ring as one of the functional substituents [1].

In attempting to obtain cyclopropane derivatives containing a 3-methoxy-2,2-dimethyl-1,3-dioxopropyl moiety instead of an aroyl group, we studied the reaction of zinc enolate **1** (obtained from the methyl ester of 4,4-dibromo-2,2-dimethyl-3-oxopentanoic acid (**2**)) with N-substituted amides of 2-oxochromene-3-carboxylic acid **3a,b**. However, we found that the reaction does not stop in the cyclopropanation step but rather we unexpectedly observe (see scheme) formation of the products of an additional intramolecular cyclization: 9c-methyl-2-R-9b,9c-dihydro-5-oxa-2-azacyclopenta[2,3]cyclopropa[1,2-*a*]naphthalene-1,3,4-triones **7a,b** (Scheme 1)

Probably in ether–ethyl acetate–THF–HMPTA medium, the zinc enolate **1** regiospecifically reacts with the electrophilic substrates **3a,b** to form the intermediates **4a,b**. Stereospecific cyclization of intermediates **4a,b** leads to synthesis of the corresponding cyclopropanation products **5a,b**, in which the amide group and the keto ester moiety are located on the same side of the plane of the three-membered ring, making additional heterocyclization possible. We may hypothesize that the amide group attacks the ketone group to form intermediate **6a,b** (which is stabilized in a process similar to acid cleavage reactions of acetoacetic ester) to form 9c-methyl-2-R-9b,9c-dihydro-5-oxa-2-azacyclopenta[2,3]cyclopropa[1,2-*a*]naphthalene-1,3,4-triones **7a,b.**

The structure of compounds **7a,b** was proven by elemental analysis data and IR and ^{1}H NMR spectroscopy.

The IR spectra include characteristic absorption bands for lactone carbonyls at 1745-1755 cm^{-1} and for lactam groups at 1695-1715 cm^{-1} and 1770-1800 cm^{-1}.

In the ^{1}H NMR spectra, we observe characteristic signals in the 1.21-1.28 ppm (s) and 3.10-3.50 ppm (s) regions, respectively belonging to protons of the methyl group and the methine proton (CH).

9c-Methyl-2-(4-methylphenyl)-9b,9c-dihydro-5-oxa-2-azacyclopenta[2,3]cyclopropa[1,2-*a*]-naphthalene-1,3,4-trione (7a). Yield 38%; mp 281-282°C. IR spectrum (vaseline oil), ν, cm^{-1}: 1715, 1755, 1800. ^{1}H NMR spectrum (100 MHz, $CDCl_3$), δ, ppm: 1.28 (3H, s, CH_3); 2.29 (3H, s, CH_3); 3.50 (1H, s, CH); 7.05-7.35 (9H, m, C_6H_4, 4-Me$C_6\underline{H}_4$). Found, %: C 71.93; H 4.47; N 4.11. $C_{20}H_{15}NO_4$. Calculated, %: C 72.06; H 4.54; N 4.20.

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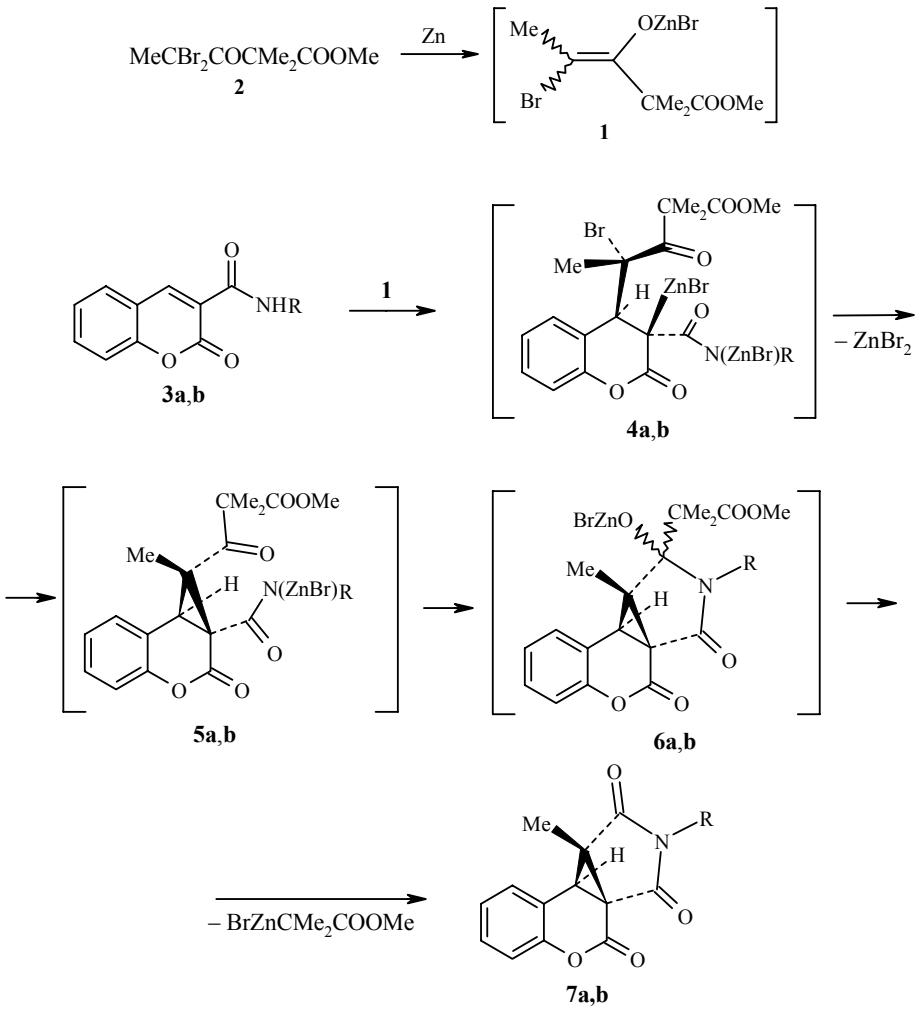
Scheme 1



3-7 a R = 4-MeC_6H_4, **b** R = CH_2Ph

2-Benzyl-9c-methyl-9b,9c-dihydro-5-oxa-2-azacyclopenta[2,3]cyclopropa[1,2-*a*]naphthalene-1,3,4-trione (7b). Yield 44%; mp 185-186°C. IR spectrum (vaseline oil), ν, cm^{-1}: 1695, 1745, 1770. ^1H NMR spectrum (100 MHz, $CDCl_3$), δ, ppm: 1.21 (3H, s, CH_3); 3.10 (1H, s, CH); 4.53 (2H, s, CH_2); 6.85-7.30 (9H, m, C_6H_4, C_6H_5). Found, %: C 71.95; H 4.48; N 4.09. $C_{20}H_{15}NO_4$. Calculated, %: C 72.06; H 4.54; N 4.20.

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