Chemistry of Heterocyclic Compounds, Vol. 40, No. 2, 2004

CYCLIZATION OF *o*-CARBOXYANILIDES OF AROYLACETIC ACIDS: A ROUTE TO A NOVEL CLASS OF HETEROCYCLIC ENAMINO KETONES

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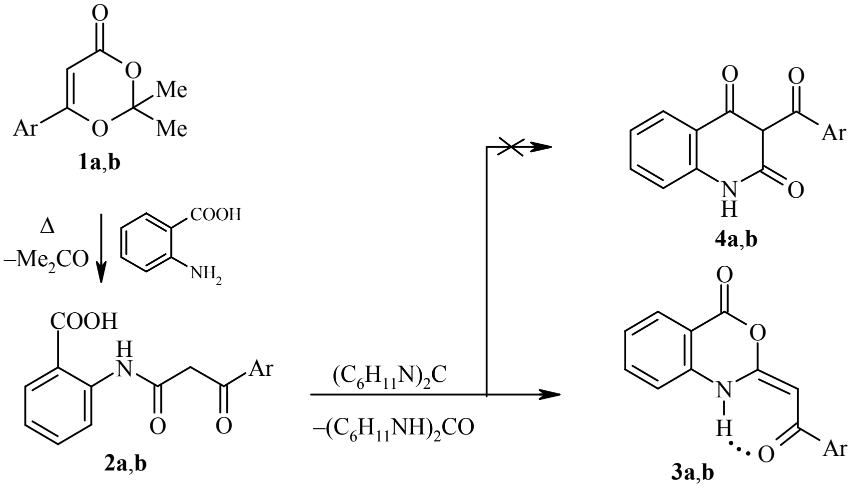
Keywords: 2-aroylmethylene-3,1-benzoxazin-4-ones, *o*-carboxyanilides of aroylacetic acids.

A convenient method for obtaining amides of aroylacetic acids is aroylacylation of amines [1] and amides [2] by aroylketenes, generated in thermolysis of 6-aryl-2,2-dimethyl-4H-1,3-dioxin-4-ones. Use of anthranilic acid as the amine is of interest because of the possibility of using the carboxyl functional group in further conversions.

In thermolysis of 6-aryl-2,2-dimethyl-4H-1,3-dioxin-4-ones **1a,b** in the presence of anthranilic acid, we obtained *o*-carboxyanilides of aroyl acetic acids **2a,b**, which undergo ring closure when treated with dicyclohexylcarbodiimide to form *E*-2-aroylmethylene-2,4-dihydro-1H-3,1-benzoxazin-4-ones **3a,b**.



1–4 a Ar = Ph, **b** Ar = *p*-MeOC$_6$H$_4$

Based on spectral data, we can eliminate the structure of the isomeric 3-aroyl-1,2,3,4-tetrahydroquinoline-2,4-diones **4a,b** for the products of intramolecular cyclization, but the described reaction is a preparative method for obtaining representatives of a novel class of heterocyclic enamino ketones.

***o*-Carboxyanilide of Benzoylacetic Acid (2a).** A solution of dioxinone **1a** (1.00 g, 4.9 mmol) and anthranilic acid (0.67 g, 4.9 mmol) in *m*-xylene (2 ml) was boiled for 10-15 min and then cooled down, and the precipitate was filtered out. Yield 1.10 g (79%); mp 177-178°C (ethanol). IR spectrum (vaseline oil), ν, cm^{-1}:

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3160 broad (NH, COOH), 1698 (COOH), 1685 broad (CONH, COPh), 1540 ("amide II"). ^{1}H NMR spectrum (400 MHz, DMSO-d$_6$), δ, ppm: 4.31 (2H, s, CH_2); 7.18-8.44 (9H, m, C_6H_4+C_6H_5); 11.26 (1H, s, NH); 13.60 (1H, br. s, COOH). Found, %: C 67.76; H 4.60; N 5.00. $C_{16}H_{13}NO_4$. Calculated, %: C 67.84; H 4.63; N 4.94.

***o*-Carboxyanilide of 4-Methoxybenzoylacetic Acid (2b).** Synthesized analogously. Yield 1.07 g (70%); mp 175-176°C (ethanol). IR spectrum (vaseline oil), ν, cm^{-1}: 3145 broad (NH, COOH), 1703 (COOH), 1670 broad (CONH, COC_6H_4), 1533 ("amide II"). ^{1}H NMR spectrum (400 MHz, DMSO-d$_6$), δ, ppm: form (A): 3.86 (3H, s, MeO); 4.22 (2H, s, CH_2); 7.05-8.44 (8H, m, $2C_6H_4$); 11.26 (1H, s, NH), 13.58 (1H, br. s, COOH). Found, %: C 65.25; H 4.80; N 4.45. $C_{17}H_{15}NO_5$. Calculated, %: C 65.17; H 4.83; N 4.47.

***E*-2-Phenacylidene-2,4-dihydro-1H-3,1-benzoxazin-4-one (3a).** A solution of anilide **2a** (0.95 g, 3.35 mmol) and dicyclohexylcarbodiimide (0.69 g, 3.35 mmol) in 1,2-dichloroethane (20 ml) was boiled for 1 h and then cooled down, and the precipitate of dicyclohexylurea was filtered out. The mother liquor was evaporated and the residue was crystallized from 2-propanol. Yield 0.89 g (100%); mp 141-142°C (2-propanol). IR spectrum (vaseline oil), ν, cm^{-1}: 3050 broad (NH in the intramolecular hydrogen bond); 1762 ($C_{(4)}$=O); 1634 broad (COPh in the intramolecular hydrogen bond). ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 5.95 (1H, s, CH); 7.37-8.15 (9H, m, C_6H_5 + C_6H_4); 14.26 (1H, s, NH). Found, %: C 72.39; H 4.15; N 5.30. $C_{16}H_{11}NO_3$. Calculated, %; C 72.45; H 4.18; N 5.28.

***E*-2-(4-Methoxybenzoylmethylene)-2,4-dihydro-1H-3,1-benzoxazin-4-one (3b).** Synthesized analogously. Yield 0.99 g (100%); mp 164-165°C (2-propanol). IR spectrum (vaseline oil), ν, cm^{-1}: 3040 broad (NH in the intramolecular hydrogen bond); 1750 ($C_{(4)}$=O), 1630 broad (COC_6H_4 in the intramolecular hydrogen bond). ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 3.88 (3H, s, MeO); 5.88 (1H, s, CH); 6.95-8.13 (8H, m, $2C_6H_4$); 14.27 (1H, s, NH). ^{13}C NMR spectrum (100 MHz, $CDCl_3$), δ, ppm: 55.48 (MeO); 83.93 ($C_{(2)}=\underline{C}H$); 114.10 ($C_{(4a)}$); 121.25-129.35 (ArH); 137.00 ($C_{(8a)}$); 162.12 ($C_{(4)}$); 162.56 ($C_{(2)}$); 177.30 ($\underline{C}OC_6H_4$). Found, %: C 69.17; H 4.48; N 4.75. $C_{17}H_{13}NO_4$. Calculated, %: C 69.15; H 4.44; N 4.74.

The research was done with the financial support of the Russian Foundation for Basic Research (grants Nos. 04-03-33024, 04-03-96033) and the Ministry of Education of the Russian Federation (grant A03-2.11-55); the NMR spectra were taken at the Ural Regional NMR Spectroscopy Center (URAL-NMR) (Russian Foundation for Basic Research grant No. 00-03-40139).

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