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SYNTHESIS OF A NEW HETEROCYCLIC SYSTEM – PYRROLO[1,2-*a*][4,1]BENZOXAZEPINE

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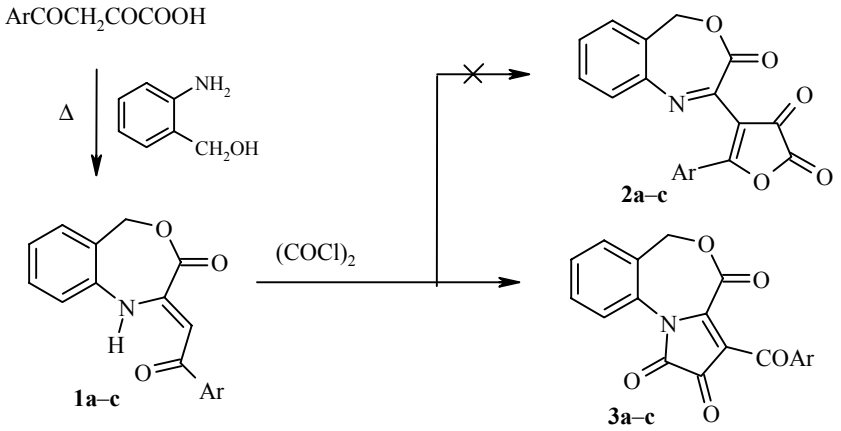
Heterocyclic enamino ketones react with oxalyl chloride to give hetereno[*a*]2,3-dihydro-2,3-pyrrolediones [1-5] or 4-heteryl-2,3-dihydro-2,3-furandiones [6]. In order to expand the data base permitting us to predict realization of one of the two pathways indicated above, we synthesized 2-phenacylidene-1,2,3,5-tetrahydro-4,1-benzoxazepin-3-ones (**1a-c**) and studied the reaction of these compounds with oxalyl chloride. The structure of substituted benzoxazepines **1a-c** is the limiting structure for realization of one of the alternative pathways of the reaction of these compounds with oxalyl chloride.

Substituted benzoxazepinones **1a-c** were obtained in the reaction of aroylpyruvic acids with *o*-aminobenzyl alcohol by a modification of our previous method [7]. The reaction of **1a-c** with oxalyl chloride under conditions used commonly for the synthesis of five-membered 2,3-dioxo heterocycles [1-6] gives 3-aroyl-2,4-dihydro-1H-pyrrolo[1,2-*a*][4,1]benzoxazepine-1,2,4-triones **3a-c** instead of the expected 2-(2-aryl-4,5-dioxo-4,5-dihydro-3-furyl)-3,5-dihydro-4,1-benzoxazepin-3-ones **2a-c**.



1-3 a Ar = Ph, **b** Ar = *p*-BrC_6H_4 , **c** Ar = *p*-MeC_6H_4

Closure of a pyrroledione ring probably occurs in this reaction due to its greater thermodynamic stability relative to the alternative furandione ring, while steric hindrance leading to closure of a furandione ring is not as significant as in our previous work [6]. This reaction is the first case reported for the construction of a new heterocyclic system of substituted pyrrolo[1,2-*a*][4,1]benzoxazepine.

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The IR spectra were obtained in vaseline oil. The ^{1}H NMR spectra were obtained in DMSO-d_6 at 400 MHz with HMDS as the internal standard.

Benzoyl-2,4-dihydro-1H-pyrrolo[1,2-*a*][4,1]benzoxazepine-1,2,4-trione (3a). A solution of *Z*-2-phenacylidene-1,2,3,5-tetrahydro-4,1-benzoxazepin-3-one (**1a**) (0.01 mmol) and oxalyl chloride (0.01 mmol) in absolute benzene (3 ml) was heated at reflux for 50 min and then cooled. The precipitate formed was filtered off. Yield of compound **3a** 3.00 g (90%); mp 213-215°C (dec., benzene). IR spectrum, ν, cm^{-1}: 1775 ($C_{(1)}$=O), 1752 ($C_{(4)}$=O), 1717 ($C_{(2)}$=O), 1651 (COC_6H_5). ^{1}H NMR spectrum (400 MHz), δ, ppm, (*J*, Hz): 5.37, 5.96 (2H, *J* = 12.8, AB system, CH_2); 7.44-7.99 (9H, m, C_6H_5 + C_6H_4). Found, %: C 68.52; H 3.41; N 4.66. $C_{19}H_{11}NO_5$. Calculated, %: C 68.47; H 3.33; N 4.20.

3-*p*-Bromobenzoyl-2,4-dihydro-1H-pyrrolo[1,2-*a*][4,1]benzoxazepine-1,2,4-trione (3b) was obtained analogously. Yield of compound **3b** 3.79 g (92%); mp 199-201°C (dec., benzene). IR spectrum, δ, cm^{-1}: 1776 ($C_{(1)}$=O), 1746 ($C_{(4)}$=O), 1723 ($C_{(2)}$=O), 1640 (COC_6H_4). ^{1}H NMR spectrum (400 MHz), δ, ppm, (*J*, Hz): 5.37, 5.94 (2H, *J* = 12.6, AB system CH_2); 7.37-7.91 (8H, m, $2C_6H_4$). Found, %: C 55.40; H 2.39; Br 19.33; N 3.36. $C_{19}H_{10}BrNO_5$. Calculated, %: C 55.36; H 2.45; Br 19.38; N 3.40.

3-*p*-Methylbenzoyl-2,4-dihydro-1H-pyrrolo[1,2-*a*][4,1]benzoxazepine-1,2,4-trione (3c) was obtained analogously. Yield of compound **3c** 2.81 g (81%); mp 203-205°C (dec., benzene). IR spectrum, δ, cm^{-1}: 1785 ($C_{(1)}$=O), 1745 ($C_{(4)}$=O), 1735 ($C_{(2)}$=O), 1640 (COC_6H_4). ^{1}H NMR spectrum (400 MHz), δ, ppm, (*J*, Hz): 2.45 (3H, s, CH_3); 5.23, 5.96 (2H, dd, *J* = 12.6, AB system CH_2); 7.16-7.88 (8H, m, $2C_6H_4$). Found, %: C 69.12; H 3.78; N 4.06. $C_{20}H_{13}NO_5$. Calculated, %: C 69.16; H 3.77; N 4.03.

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