

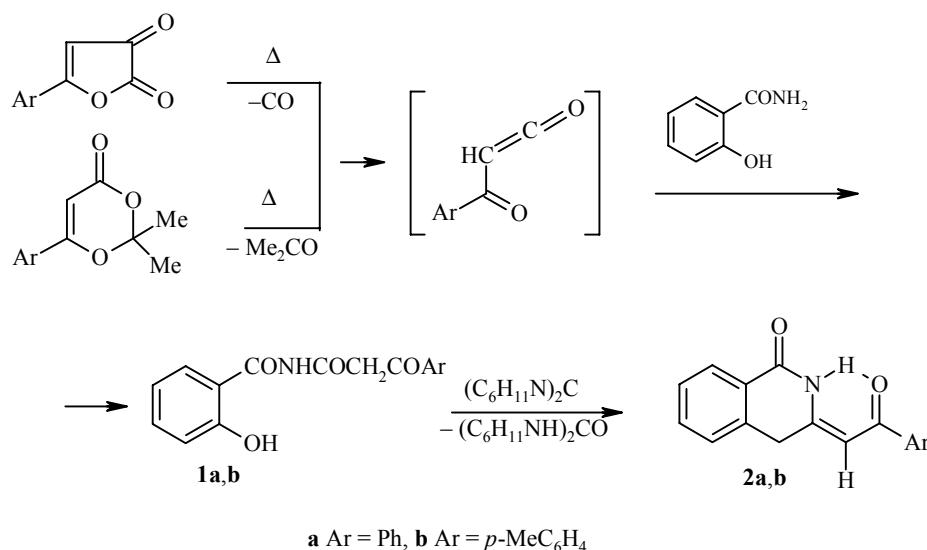
***E*-2-AROYLMETHYLENE-3,4-DIHYDRO-2H-1,3-BENZOXAZIN-4-ONES – A NEW CLASS OF HETEROCYCLIC ENAMINO KETONES**

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**Keywords:** 2-arylmethylene-1,3-benzoxazin-4-ones, *o*-hydroxybenzoylamides, aroylacetic acids.

Aroylketenes generated by the thermal decarbonylation of 5-aryl-2,3-dihydro-2,3-furandiones react with salicylamide regioselectively to give *N*-aroylacetylation products, namely, *N*-*o*-hydroxybenzoylamides of aroylacetic acids **1a** and **1b**. This reaction does not proceed without thermolysis [1]. Evidence for the structure of the products may be found in their formation from 6-aryl-2,2-dimethyl-4H-1,3-dioxin-4-ones, which also generate ketenes upon thermolysis, and salicylamide. Attempts to effect the intramolecular cyclizations of amides **1a** and **1b** by heating were unsuccessful and led to decomposition of the reaction system.

We have developed a preparative method for the intramolecular cyclization of amides **1a** and **1b** by the action of dicyclohexylcarbodiimide with the production of dicyclohexylurea and formation of *E*-2-arylmethylene-3,4-dihydro-2H-1,3-benzoxazin-4-ones **2a** and **2b**, which feature intramolecular hydrogen bonding between the N<sub>(3)</sub>H group and carbonyl oxygen atom of the side-chain.



We should note that benzoxazinone **2** are members of a new class heterocyclic enamino ketones. A search for such compounds using the CAS and Beilstein data bases was unsuccessful.

***E*-2-Phenacylidene-3,4-dihydro-2H-1,3-benzoxazin-4-one (2a).** A solution of amide **1a** (0.50 g, 1.765 mmol) and dicyclohexylcarbodiimide (0.36 g, 1.765 mmol) in absolute dioxane (10 ml) was heated at reflux for 1 h and cooled. The precipitate of dicyclohexylurea was filtered off and the mother liquor was evaporated. The residue was crystallized from benzene to give 0.40 g (85%) of compound **2a**; mp 198-199°C (benzene). IR spectrum (vaseline oil),  $\nu$ ,  $\text{cm}^{-1}$ : 1700 ( $\text{C}_{(4)}=\text{O}$ ), 1630 br (COPh).  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ),  $\delta$ , ppm: 6.05 (1H, s, CH); 7.24-8.10 (9H, m, ArH); 13.29 (1H, s, NH). Mass spectrum,  $m/z$  ( $I_{\text{rel}}$ , %): 265 (68)  $[\text{M}]^+$ . Found, %: C 72.44; H 4.20; N 5.28.  $\text{C}_{16}\text{H}_{11}\text{NO}_3$ . Calculated, %: C 72.45; H 4.18; N 5.28; M 265.

***E*-2-*p*-Toluoylmethylidene-3,4-dihydro-2H-1,3-benzoxazin-4-one (2b)** was synthesized analogously. The yield of **2b** was 0.40 g (82%); mp 185-186°C (benzene). IR spectrum (vaseline oil),  $\nu$ ,  $\text{cm}^{-1}$ : 1705 ( $\text{C}_{(4)}=\text{O}$ ), 1640 br (COAr).  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ),  $\delta$ , ppm: 2.40 (3H, s, Me); 6.00 (1H, s, CH); 7.21-8.08 (8H, m, ArH); 13.29 (1H, s, NH).  $^{13}\text{C}$  NMR spectrum (100 MHz,  $\text{CDCl}_3$ ),  $\delta$ , ppm: 21.53 (Me), 81.09 ( $\text{C}_{(2)}=\underline{\text{C}}\text{H}$ ), 116.35 ( $\text{C}_{(4a)}$ ), 125.20-142.91 (Ar), 153.88 ( $\text{C}_{(8a)}$ ), 156.78 ( $\text{C}_{(2)}$ ), 160.26 ( $\text{C}_{(4)}$ ), 189.61 ( $\underline{\text{C}}\text{OC}_6\text{H}_4$ ). Found, %: C 73.18; H 4.79; N 5.03.  $\text{C}_{17}\text{H}_{13}\text{NO}_3$ . Calculated, %: C 73.11; H 4.69; N 5.01.

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