INTERACTION OF ESTERS OF β-AROYLACRYLIC ACIDS WITH o-PHENYLENEDIAMINES AND 1,2-DIAMINO-4-PHENYL-IMIDAZOLE

N. N. Kolos¹, L. Yu. Kovalenko¹, S. V. Shishkina²,
O. V. Shishkin², and I. S. Konovalova²

3-Phenacylquinoxalin-2-ones were synthesized by the reaction of the ethyl esters of β-aroylacrylic acids with o-phenylenediamines, while interaction with 1,2-diamino-4-phenylimidazole gave ethyl 7-amino-2-aryl-5-phenyl-3,4-dihydroimidazo[1,5-b]pyridazine-4-carboxylates. Their chemical properties have been investigated.

Keywords: dihydroimidazo[1,5-b]pyridazine-4-carboxylates, o-phenylenediamines, 1,2-diamino-4-phenylimidazole, β-aroylacrylic acid ethyl esters, chemical properties, cyclocondensation.

β-Aroylacrylic acids are convenient polyelectrophilic reagents in the synthesis of heterocycles, for which the addition reaction of N-, S-, P-, or C-nucleophiles occurs exclusively at the α-carbonyl-electrophilic center of the molecule [1-3]. The products of C-nucleophilic addition were successfully isolated on interaction of the acids with 1,2-diamino-4-phenylimidazole, however cyclization of the intermediates is accompanied by decarboxylation and aromatization, which enabled the preparation only of heteroaromatic derivatives of imidazopyridazine [4]. This limitation was taken off when using N-arylamides of aroylacrylic acids in reaction with the amine indicated [5].

With the aim of broadening the synthetic potential of β-aroylacrylic acids, the behavior of their ethyl esters 1a-f was studied in reaction with o-phenylenediamines 2a,b and 1,2-diamino-4-phenylimidazole (3). Several electrophilic centers are present in the molecules of α,β-unsaturated γ-keto esters 1, viz. atoms C(2) and C(4) and the carbon atom of the ester group, which is hopeful for many reaction routes with nucleophilic reagents.

The initial γ-keto esters 1a-f were synthesized by known literature methods [6-8]. Their interaction (in the example of compounds 1a,b) with diamine 2a in methanol leads to 3-phenacylquinoxalin-2-ones 4a,b, isolated in high yield. The latter were obtained previously by the reaction of the appropriate β-aroylacrylic acids with o-PDA (o-phenylenediamine) [9].
1a–f + 3 → 6

1 a R = H, b R = 4-Me, c R = 4-Cl, d R = 4-Br, e R = 4-OMe, f R = 2,4-Me₂; 2 a R¹ = Me, b R¹ = NO₂; 4 a R = R¹ = H, b R = 4-Me, R¹ = H; c R = 6-NO₂, R¹ = 4-Cl; 5c R = 7-NO₂, R¹ = 4-Cl; 7 a R = H, b R = 4-Me, c R = 4-Cl, d R = 4-Br, e, f R = 4-OMe, g R = 2,4-Me₂