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NEW SYNTHESIS OF THE [1,3]THIAZOLO-[3',2':2,3][1,2,4]TRIAZINO[5,6-*b*]INDOLE SYSTEM

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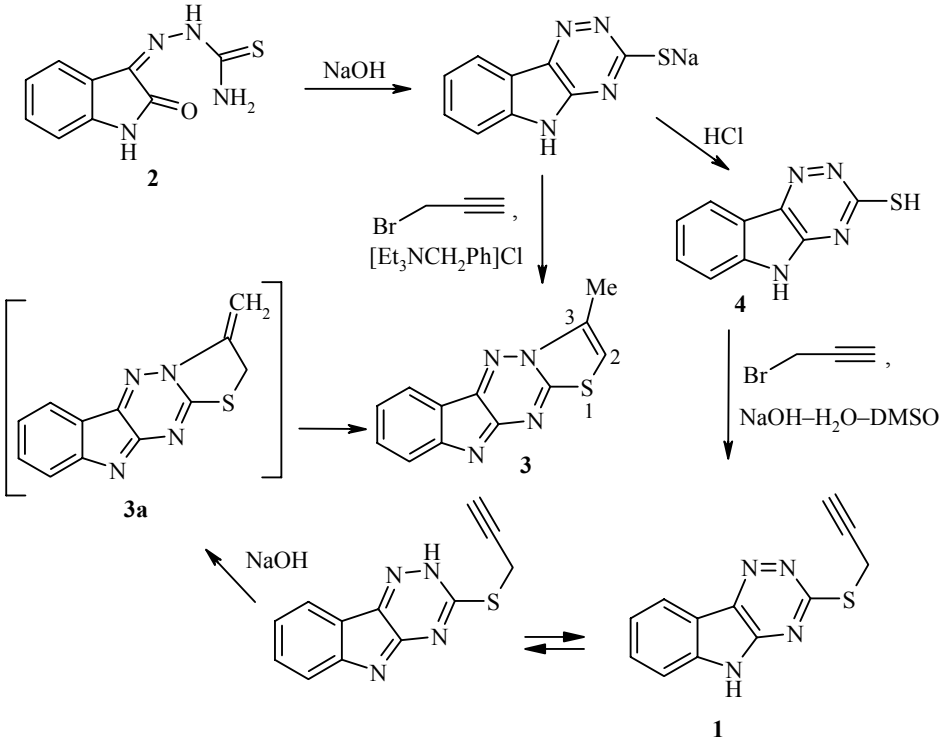
Tomchin [1] was the first to report the preparation of the new 2,3-diphenyl[1,3]thiazolo[3',2':2,3]-[1,2,4]triazino[5,6-*b*]indole system by the reaction of 3-benzoylphenylmethylthio[1,2,4]triazino[5,6-*b*]indole with PPA but no spectral evidence was given for the formation of this product.

In an attempt to obtain 3-propargylthio-5H-[1,2,4]triazino[5,6-*b*]indole (**1**) by a one-pot synthesis from isatin-β-thiosemicarbazone (**2**) by the action of aqueous alkali and propargyl bromide under phase-transfer



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catalysis conditions, we unexpectedly obtained another representative of this heterocyclic system, namely, 3-methyl[1,3]thiazolo[3',2':2,3][1,2,4]triazino[5,6-*b*]indole (**3**). Triazinoindole **1** is formed by the reaction of 5H-[1,2,4]triazino[5,6-*b*]indole-3-thiol (**4**) with propargyl bromide in the NaOH-H_2O-DMSO superbase medium [2]. Triazinoindole **3** is probably formed by intramolecular cyclization of triazinoindole **1** through intermediate **3a**. Thus, heating triazinoindole **1** in aqueous NaOH at reflux leads to triazinoindole **3**.

The ^{1}H NMR spectrum of triazinoindole **3** shows singlets for the methyl group protons at 2.64 ppm and for H-2 at 7.47 ppm. The mass spectrum has a molecular ion peak (M^+ 240).

The ^{1}H NMR spectrum was taken on a Bruker spectrometer at 400 MHz in DMSO-d_6 with TMS as the internal standard. The electron impact mass spectra were taken on a Hewlett-Packard GC/MS computer with an HP-5890 gas chromatograph at 70 eV.

3-Propargylthio-5H-[1,2,4]triazino[5,6-*b*]indole (1). Propargyl bromide (0.152 g, 1 mmol) was added to a mixture of indolethiol **4** (0.202 g, 1 mmol) and NaOH (0.04 g, 1 mmol) in DMSO (10 ml). The reaction mixture was stirred for 1.5 h at room temperature. Then, water (50 ml) was added. The colorless light brown precipitate was filtered off, washed with water, and dried to give 0.202 g (84%) triazinoindole **1**; mp ~173°C. ^{1}H NMR spectrum, δ, ppm: 3.17 (1H, s, CH≡); 4.13 (2H, s, S–CH_2); 7.45, 7.60, 7.71, 8.31 (4H, benzene ring).

3-Methyl[1,3]triazolo[3',2':2,3][1,2,4]triazino[5,6-*b*]indole (3). A. A solution of thiosemicarbazone **2** (0.5 g, 2 mmol) [3] in 1 N NaOH (40 ml) was heated at reflux for 3 h. Then, propargyl bromide (0.24 g, 2 mmol) and triethylbenzylammonium chloride (50 ml) as the phase-transfer catalyst were added and the mixture was stirred for 1.5 h at room temperature. The red precipitate was filtered off, washed with water, and dried to give triazinoindole **3** in 43% yield; mp 140°C (ethanol, dec.). ^{1}H NMR spectrum, δ, ppm: 2.64 (3H, s, CH_3); 7.47 (1H, s, H-2); 7.33, 7.69, 8.23 (4H, benzene ring). Found, %: C 59.74; H 3.31; N 23.42. $C_{12}H_8N_4S$. Calculated, %: C 59.98; H 3.36; N 23.32.

B. A solution of triazinoindole **1** (0.1 g, 0.4 mmol) in 1 N NaOH (5 ml) was heated at reflux for 1.5 h. The red precipitate was filtered off, washed with water, and dried to give triazinoindole **3** in 60% yield. This product was identical to the product obtained by method A and the melting point of a mixed sample was not depressed.

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