

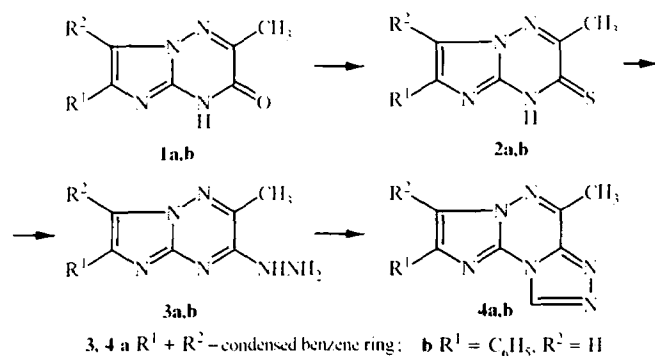
**SYNTHESIS OF 2-METHYL-1,2,4-
TRIAZOLO[4,3-*d*]-1,2,4-TRIAZINO[2,3-*a*]-
BENZIMIDAZOLE AND 2-METHYL-9-
PHENYLIMIDAZO[1,2-*b*]-1,2,4-
TRIAZOLO[4,3-*d*]-1,2,4-TRIAZINE**

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Keywords: 2-methyl-1,2,4-triazolo[4,3-*d*]-1,2,4-triazino[2,3-*a*]benzimidazole, imidazo[1,2-*b*]1,2,4-triazolo[4,3-*d*]-1,2,4-triazine, hydrazine hydrate

Boiling (4 h) of 4H-2-methyl-1,2,4-triazino[2,3-*a*]benzimidazol-3-one (**1**) [1] with phosphorus pentasulfide in dioxane gave the thioanalog **2a**. The latter was synthesized in 52% yield from lactam **1** and phosphorus pentasulfide by boiling for 3 h in pyridine. 3-Hydrazino-2-methyl-1,2,4-triazino[2,3-*a*]benzimidazole (**3a**) was obtained by the reaction of thione **2a** with hydrazine hydrate on boiling for 1.5 h in ethanol. The previously unknown 2-methyl-1,2,4-triazolo[4,3-*d*]-1,2,4-triazino[2,3-*a*]benzimidazole (**4a**) was synthesized by the condensation of the hydrazine derivative **3a** (2 mol) and formic acid (150 mol) on boiling for 4 h.

Compound **3b** was obtained analogously from 4H-2-methyl-6-phenylimidazo[1,2-*b*]-1,2,4-triazine-3-thione **2b** [2] and hydrazine hydrate, and was cyclized by boiling for 2 h in formic acid to synthesize 2-methyl-9-phenylimidazo[1,2-*b*]-1,2,4-triazolo[4,3-*d*]-1,2,4-triazine (**4b**) for the first time.



EXPERIMENTAL

4H-2-Methyl-1,2,4-triazino[2,3-*a*]benzimidazole-3-thione (2a). Yield 63%; mp 324-325°C (DMF). *R*_f 0.57. IR spectrum (KBr): 1090 (C=O); 3200 cm⁻¹ (N-H). UV spectrum (propan-2-ol), λ_{max} (log ε): 235 (4.16); 250 (3.81); 310 (4.27). Found, %: C 55.59; H 3.96; N 25.62. C₁₀H₈N₄S. Calculated, %: C 55.54; H 3.73; N 25.90.

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Compound 3a. Yield 55%; mp >350°C (DMF). R_f 0.48. IR spectrum (KBr): 3070-3230 cm^{-1} (N-H). Found, %: C 56.25; H 4.89; N 39.51. $\text{C}_{11}\text{H}_{10}\text{N}_6$. Calculated, %: C 56.07; H 4.70; N 39.23.

3-Hydrazino-2-methyl-6-phenylimidazo[1,2-*b*]-1,2,4-triazine (3b). Yield 62%; mp 225-226°C (propan-2-ol-DMF, 1:1). R_f 0.28. IR spectrum (KBr): 3230-3310 cm^{-1} (N-H). Found, %: C 60.01; H 5.28; N 34.76. $\text{C}_{12}\text{H}_{12}\text{N}_6$. Calculated, %: C 59.99; H 5.03; N 34.98.

Compound 4a. Yield 53%; mp 304-305°C (DMF). R_f 0.43. Mass spectrum, m/z (I_{rel} , %): 225 (15), M^+ 224 (100), $[\text{M}-\text{HCN}]^+$ 197 (5), $[\text{M}-\text{C}_2\text{H}_2\text{N}_1]^+$ 156 (90), $[\text{M}-\text{C}_2\text{H}_2\text{N}_1-\text{HCN}]^+$ 129 (8); benzimidazole fragment 116 (7), 104 (35), 90 (38), 77 (14). UV spectrum (propan-2-ol), λ_{max} ($\log \epsilon$): 260 (4.37); 298 (3.91). Found, %: C 58.71; H 3.45; N 37.73. $\text{C}_{11}\text{H}_8\text{N}_6$. Calculated, %: C 58.92; H 3.60; N 37.48.

Compound 4b. Yield 72%; mp 249-250°C (propan-2-ol-DMF, 1:1). R_f 0.74. Mass spectrum, m/z (I_{rel} , %): 251 (15), M^+ 250 (98), $[\text{M}-\text{C}_2\text{H}_2\text{N}_1]^+$ 129 (15), $[\text{M}-\text{C}_2\text{H}_2\text{N}_1-\text{HCN}]^+$ 102 (12); benzimidazole fragment 156 (5), 116 (7), 103 (100), 77 (21). Found, %: C 62.41; H 4.12; N 33.79. $\text{C}_{11}\text{H}_{10}\text{N}_6$. Calculated, %: C 62.39; H 4.03; N 33.58.

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