

SHORT
COMMUNICATIONSSynthesis of 6-Butyl-7-methylidene-8-phenyl-5*H*-pyrrolo-[3,4-*d*]tetrazolo[1,5-*a*]pyrimidin-5-oneV. L. Gein^a, O. S. Panova^a, E. P. Tsypliyakova^a, L. I. Varkentin^a,
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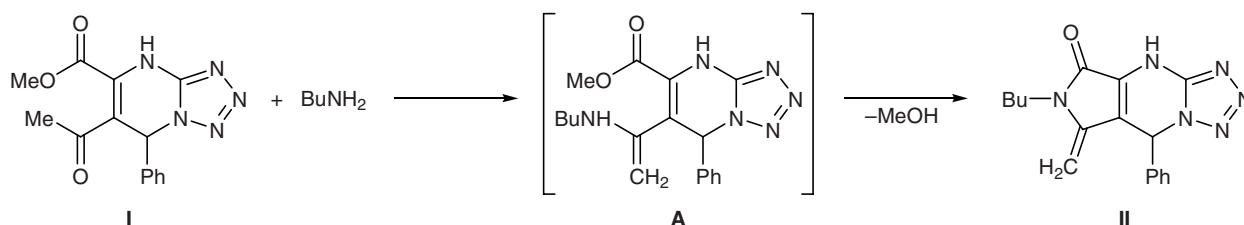
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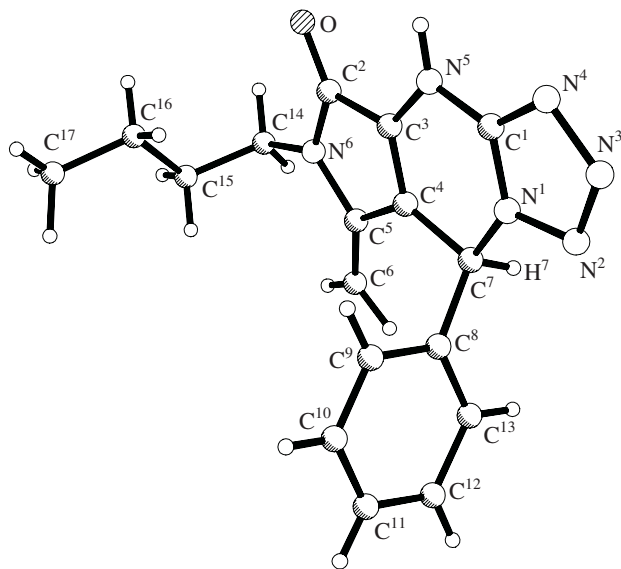
We have found that methyl 6-acetyl-4,7-dihydro-7-phenyltetrazolo[1,5-*a*]pyrimidine-5-carboxylate (**I**) reacts with an equimolar amount of butylamine at 130–150°C to give in 20–30 min 6-butyl-7-methylidene-8-phenyl-5*H*-pyrrolo[3,4-*d*]tetrazolo[1,5-*a*]pyrimidin-5-one (**II**). Presumably, in the first stage intermediate amine **A** is formed, and its enamino tautomer undergoes intramolecular cyclization to compound **II**. The latter was isolated as a yellow crystalline substance which is insoluble in water and ethanol, soluble in glacial acetic acid and acetonitrile on heating, and readily soluble in DMSO and DMF.

Compound **II** displayed in the IR spectrum absorption bands belonging to stretching vibrations of the lactam carbonyl group (1692 cm⁻¹), secondary amino group (3144 cm⁻¹), and double C=C bonds (1632 cm⁻¹). Its ¹H NMR spectrum contained signals from aromatic protons and protons in the butyl group, doublets at δ 4.43 and 4.95 ppm (*J* = 2.5 Hz) from protons in the exocyclic methylene group, NH signal at δ 11.73 ppm, and a singlet at δ 7.02 ppm from the 8-H proton. In the mass spectrum of **II** we observed the molecular ion peak [*M*]⁺ with *m/z* 322 and fragment ion peaks with *m/z* 294 [*M* – CO]⁺, 245 [*M* – Ph]⁺, and 77 [Ph]⁺, which are consistent with the assigned structure.

By slow crystallization from acetonitrile we succeeded in obtaining a single crystal of compound **II** suitable for X-ray analysis (see figure). The tricyclic fragment of molecule **II** is planar. The double bonds therein are localized with no appreciable conjugation effect. All bond lengths and bond angles have their usual values. Molecules **II** in crystal are linked through intermolecular hydrogen bonds N⁵–H⁵...N⁴, giving rise to centrosymmetric dimers. The distance N⁵...N⁴ is 2.908 Å, indicating that the intermolecular hydrogen bond is not very strong.

6-Butyl-7-methylidene-8-phenyl-5*H*-pyrrolo-[3,4-*d*]tetrazolo[1,5-*a*]pyrimidin-5-one (II**).** A mixture of 5 mmol of ester **I** [1] and 5 mmol of butylamine was heated at 130–150°C until gaseous products no longer evolved (for 20–30 min). After cooling, the mixture was treated with ethanol, and the precipitate was filtered off and recrystallized from acetonitrile. Yield 0.5 g (31%), mp 196–198°C. IR spectrum, ν, cm⁻¹: 1692 (CO), 3144 (NH), 1632 (CH₂=). ¹H NMR spectrum, δ, ppm: 4.43 d (1H, CH₂=, *J* = 2.5 Hz), 4.95 d (1H, CH₂=, *J* = 2.5 Hz), 7.02 s (1H, CH), 11.73 s (1H, NH), 7.41 m (5H, C₆H₅), 0.87 m (3H, CH₃), 1.25 m (2H, 3'-H), 1.46 m (2H, 2'-H), 3.57 m (2H, 1'-H). Found, %: C 63.22, 63.45; H 5.51, 5.74;





Structure of the molecule of 6-butyl-7-methylidene-8-phenyl-5H-pyrrolo[3,4-d]tetrazolo[1,5-a]pyrimidin-5-one (**II**) according to the X-ray diffraction data.

N 25.95, 26.19. C₁₇H₁₈N₆O. Calculated, %: C 63.34; H 5.63; N 26.07.

The IR spectrum was recorded on a Specord M-80 spectrometer from a sample of **II** dispersed in mineral oil. The ¹H NMR spectra were measured on a Varian Mercury-300 (300.056 MHz) and Bruker DRX-500 (500.13 MHz) instruments using DMSO-*d*₆ as solvent and TMS as internal reference. The mass spectrum (electron impact, 70 eV) was obtained on a Finnigan MAT INCOS-50 mass spectrometer.

A set of experimental reflections was acquired on a KM-4 automatic four-circle diffractometer with χ -geometry (monochromatized MoK α irradiation, $\omega/2\theta$ scanning to $2\theta \leq 50.14^\circ$). Monoclinic crystals with the following unit cell parameters: $a = 7.815(2)$, $b = 3.291(3)$, $c = 15.766(3)$ Å; $\beta = 90.96(3)^\circ$; $V = 1637.4(6)$ Å³; $M = 322.37$; $d_{\text{calc}} = 1.308$ g/cm³; $Z = 4$; space group $P2(1)/c$. Total of 2864 independent reflections ($R_{\text{int}} 0.0208$) were measured. No correction for absorption was introduced ($\mu = 0.087$ mm⁻¹). The structure was solved by the direct method using SIR92 program [2], followed by a series of calculations of electron density maps. The positions of hydrogen atoms were set on the basis of geometry considerations. Full-matrix anisotropic refinement of the positions of non-hydrogen atoms by the least-squares procedure using SHELXL-97 program [3] was complete at $R_1 = 0.0460$, $wR_2 = 0.1163$ [from 1368 reflections with $I \geq 2\sigma(I)$]; goodness of fit 0.889.

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