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# LETTERS TO THE EDITOR

## SYNTHESIS OF NEW HETEROCYCLIC SYSTEMS CONTAINING THE BICYCLO-[3.3.1]NONANE FRAGMENT

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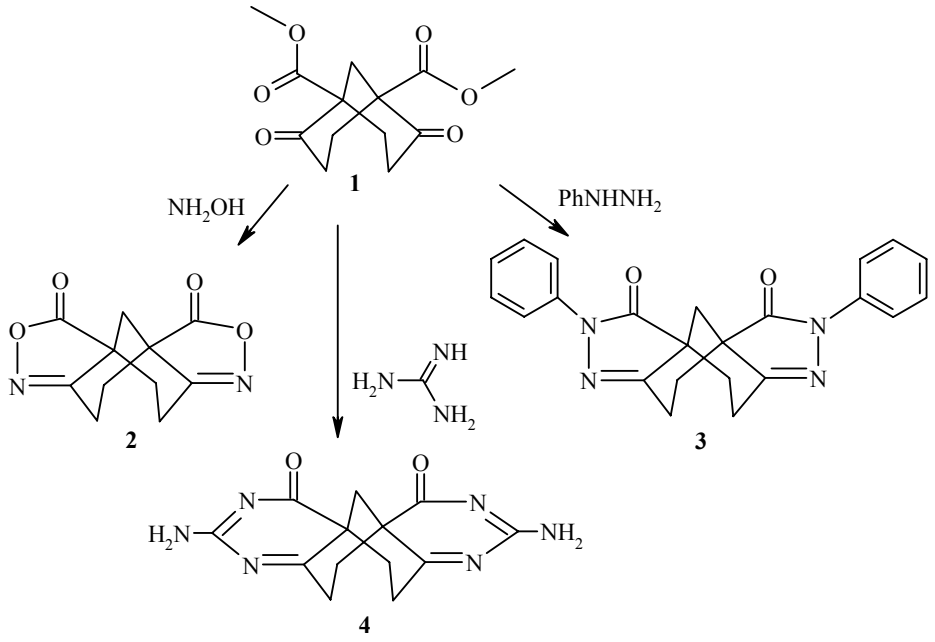
**Keywords:** bicyclo[3.3.1]nonane, 4,5-dihydro-5-isoxazolone, 4,5-dihydro-1H-5-pyrazolone, 4,5-dihydro-4-pyrimidinone, β-keto esters, condensation.

In recent decades there has been a constant increase in compounds capable of forming supramolecular structures similar to those in biology [1]. According to [2] these properties are promoted by the presence of polar heterocyclic fragments condensed with the bicyclo[3.3.1]nonane skeleton. A molecule with such a form should be possible to form spiral supramolecular structures.

The new derivatives **2-4** were synthesized by condensation of the keto ester **1** (racemate) with hydroxylamine, guanidine, or phenylhydrazine.

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Absorptions of carbonyl and imine groups were observed in the IR spectra of compounds **2-4**. In the $^1$H NMR spectra only multiplet, characteristic of the bicyclo[3.3.1]nonane fragment, and signals of the phenyl and amino group protons (**3** and **4** respectively). Compound **1** was synthesized from the Meerwein ester by a published method [3].

IR spectra of nujol mulls were recorded with a Perkin-Elmer FT-IR Spectrum BX II spectrometer, $^1$H and $^{13}$C NMR spectra were recorded with a Varian-Unity Inova machine (300 and 75 MHz respectively) with TMS as internal standard.

**6,13-Dioxo-5,12-diazatetracyclo[6.6.1.0$^{1,11}$.0$^{4.8}$]pentadeca-4,11-diene-7,14-dione (2).** A solution of ketoester **1** (0.135 g, 0.5 mmol) and hydroxylamine hydrochloride (1 mmol) in ethanol (10 ml) was boiled for 12 h, cooled, the precipitate was filtered off, and recrystallized from ethanol to give compound **2** (0.056 g, 49%), mp > 350°C. IR spectrum, ν, cm$^{-1}$: 1792, 1775 (C=O), 1619 (C=N). $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 1.94-2.36 (4H, m, $CH_2$); 2.33 (2H, s, $CH_2$); 2.82-3.10 (4H, m, $CH_2$). $^{13}$C NMR spectrum (DMSO-$d_6$), δ, ppm: 178.82 (CO); 170.09 (CN); 46.90 (C); 36.57 ($CH_2$); 30.56 ($CH_2$); 23.04 ($CH_2$). Found, %: C 56.64; H 4.25; N 12.20. $C_{11}H_{10}N_2O_4$. Calculated, %: C 56.41; H 4.30; N 11.96.

**6,13-Diphenyl-5,6,12,13-tetrazatetracyclo[6.6.1.0$^{1,11}$.0$^{4.8}$]pentadeca-4,11-dien-7,14-dione (3)** was synthesized analogously to compound **2** by heating compound **1** with phenylhydrazine in acetic acid (5 ml) for 3 h at 70°C, extraction with dichloromethane, and recrystallization from hexane–toluene to give compound **3** (65%), mp> 350°C. IR spectrum, ν, cm$^{-1}$: 3424 (NH), 1713, 1702 (C=O), 1620 (C=N). $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm (*J*, Hz): 2.02-2.23 (4H, m, $CH_2$); 2.10 (2H, s, $CH_2$); 2.82-3.17 (4H, m, $CH_2$); 7.24 (2H, t, *J* = 9, H Ar); 7.48 (4H, t, *J* = 9, H Ar); 7.89 (4H, t, *J* = 9, H Ar). $^{13}$C NMR spectrum (DMSO-$d_6$), δ, ppm: 174.28 (CO); 164.74 (CN); 138.71; 129.67, 125.61 and 119.01 (C Ar); 51.18 (C); 38.49 ($CH_2$); 31.33 ($CH_2$); 25.31 (C). Found, %: C 72.04; H 5.17; N 14.44. $C_{23}H_{20}N_4O_2$. Calculated, %: C 71.86; H 5.29; N 14.57.

**6,14-Diamino-5,7,13,15-tetrazatetracyclo[7.7.1.0$^{1,12}$.0$^{4,8}$]pentadeca-4,6,12,14-tetren-8,16-dione (4)** was synthesized analogously to **2**, using guanidine carbonate. After crystallization from DMF the yield of compound **4** was 53%, mp > 350°C. IR spectrum, ν, cm$^{-1}$: 3400 and 3206 ($NH_2$), 1689 (C=O), 1653 and 1578 (C=N). $^1$H NMR spectrum ($CF_3COOD$ ), δ, ppm (*J*, Hz): 2.38 (2H, s, $CH_2$); 2.42-3.50 (4H, m, $CH_2$); 4.06-4.42 and 6.01-6.12 (4H, m, $CH_2$); 4.19 (2H, s, $CH_2$). $^{13}$C NMR spectrum ($CF_3COOD$), δ, ppm: 171.69 (CO), 150.87 (CN); 128.04 (NCN); 46.95 (C); 41.63 ($CH_2$); 33.34 ($CH_2$); 26.68 (C). Found, %: C 54.86; H 4.78; N 28.99. $C_{13}H_{14}N_6O_2$. Calculated, %: 54.54; H 4.93; N 29.35.

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