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SIMPLE SYNTHESIS OF 1,2-DIHYDRO-5,6-TRI(TETRA)METHYLENESPIRO-(CYCLOPENTANE(CYCLOHEXANE)-2-THIENO-[2,3-*d*]PYRIMIDINE-4(3H)-THIONES)

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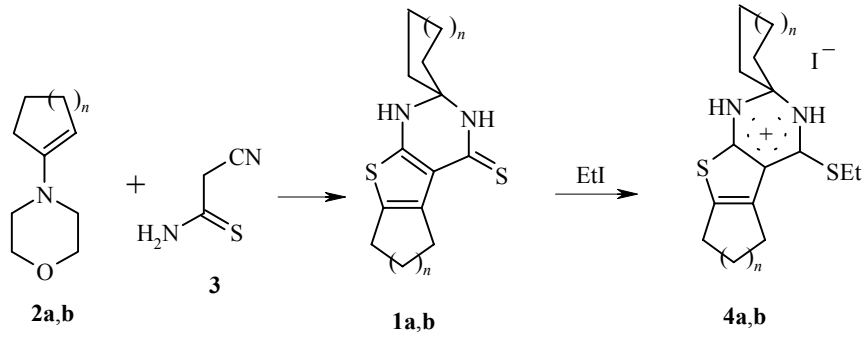
Keywords: 1,2-dihydro-5,6-tri(tetra)methylenespiro(cyclopentane(cyclohexane)-2-thieno[2,3-*d*]pyrimidine-4(3H)-thiones), cyanothioacetamide, N-(1-cycloalkenyl)morpholines, alkylation, condensation.

A novel spiro-substituted heterocyclic system, 1,2-dihydro-5,6-tetramethylenespiro(cyclohexane-2-thieno[2,3-*d*]pyrimidine-4(3H)-thione) (**1**) was obtained for the first time by condensation of cyclohexanone with cyanothioacetamide and sulfur [1]. We recently observed formation of this compound upon dimerization of cyclohexylidene cyanothioacetamide [2]. In this work, we show a third convenient route to potentially biologically active spiro-substituted nitrogen-containing heterocycles **1** [3], consisting of a one-pot synthesis for these compounds from N-(1-cycloalkenyl)morpholines **2** and cyanothioacetamide **3** in ethanol at 20°C. Upon alkylation of compound **1b** by ethyl iodide in DMF, we obtained thioether **4**. The structure of thione **1b**, the mechanism for the formation of which is under study, was proven by X-ray diffraction (the detailed data will be published later).



1, **2**, **4** **a** $n = 1$; **b** $n = 2$

The ^{1}H NMR spectra were taken on a Bruker DRX 500 (500 MHz) in DMSO-d_6.

1,2-Dihydro-5,6-trimethylenespiro(cyclopentane-2-thieno[2,3-*d*]pyrimidine-4(3H)thione) (1a). Yield 66%; mp 227-229°C (alcohol). ^{1}H NMR spectrum, δ, ppm: 8.90 (1H, br. s, NH); 7.90 (1H, br. s, NH); 2.93 (2H, m, CH_2); 2.32 (2H, m, CH_2); 1.14-1.85 (10H, m, $(CH_2)_5$). Found, %: C 58.84; H 5.91; N 10.45. $C_{13}H_{16}N_2S_2$. Calculated, %: C 59.05; H 6.10; N 10.60.

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1,2-Dihydro-5,6-tetramethylenespiro(cyclohexane-2-thieno[2,3-*d*]pyrimidine-4(3H)-thione) (1b). Yield 72%; mp 255-256°C (DMF). ^{1}H NMR spectrum, δ, ppm: 8.62 (1H, br. s, NH); 7.84 (1H, br. s, NH); 2.95 (2H, m, CH_2); 1.91 (2H, m, CH_2); 1.13-1.82 (14H, m, $(CH_2)_7$). Mass spectrum, *m*/*z* (I_{rel}, %): 292 (84) $[M]^+$, 293 (18) $[M+1]^+$, 294 (9) $[M+2]^+$, 259 (36), 249 (100), 236 (41), 167 (19), 81 (45), 53 (38), 41 (62). Found, %: C 61.48; H 6.72; N 9.67. $C_{15}H_{20}N_2S_2$. Calculated, %: C 61.60; H 6.81; N 9.58.

1,2-Dihydro-5,6-tetramethylene-4-ethylthiospiro(cyclohexane-2-thieno-[2,3-*d*]pyrimidinium Iodide (4). Yield 82%; mp 129-131°C (alcohol). ^{1}H NMR spectrum, δ, ppm (*J*, Hz); 9.72 (1H, br. s, NH); 8.88 (1H, br. s, NH); 3.40 (2H, q, *J* = 7.30, SCH_2); 2.68 (2H, m, CH_2); 2.54 (2H, m, CH_2); 2.11 (2H, m, CH_2); 1.92 (2H, m, CH_2); 1.53-1.88 (10H, m, $(CH_2)_5$); 1.38 (3H, t, *J* = 5.60, CH_3). Mass spectrum, *m*/*z* (I_{rel}, %): 320 (46) $[M]^+$, 291 (22), 277 (100), 264 (11), 128 (6). Found, %: C 45.30; H 5.71; N 6.14. $C_{17}H_{26}IN_2S_2$. Calculated, %: C 45.43; H 5.83; N 6.23.

REFERENCES

1. K. Gewald and R. Schindler, *J. Pract. Chem.*, **332**, 223 (1990).
2. A. D. Dyachenko, S. M. Desenko, V. D. Dyachenko, and V. P. Litvinov, in: *Abstracts, First All-Russian Conference on Heterocyclic Chemistry, In Memory of A. N. Kost* [in Russian], Suzdal' (2000), p. 172.
3. V. V. Kuznetsov, *Khim.-Farm. Zh.*, No. 7, 61 (1991).