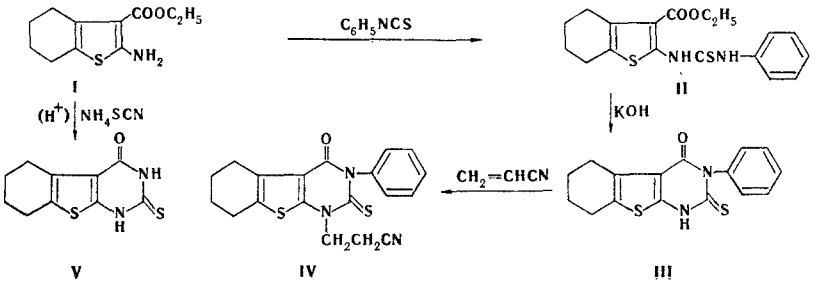
SYNTHESIS OF CYCLOHEXENO[1',2' : 2,3]THIENO[4,-5-e]-1,3H-PYRIMIDIN-4-ONE-2-THIONE AND SOME OF ITS DERIVATIVES

S. M. Khripak, A. A. Dobosh, and I. V. Smolanka

UDC 547.735+547.853

In order to synthesize various condensed heterocyclic systems [1, 2], we studied the reaction of 2-amino-3-ethylcarboxycyclohexeno[b]thiophene [3] (I) with phenyl isothiocyanate. In this case, we obtained 2-(3'-phenylthioureido)-3-ethylcarboxycyclohexeno[b]thiophene (II), which cyclizes to III on treatment with potassium hydroxide. Compound III reacts with acrylonitrile to give N-cyanoethyl derivative IV. Compound V was also synthesized from I.



Preliminary data from an investigation of the physiological activity of these and similarly constructed substances indicated they have high and selective bactericidal activity.

EXPERIMENTAL

2-(3'-Phenylthioureido)-3-ethylcarboxycyclohexeno[b]thiophene (II). This compound, with mp 184-185° (from dioxane), was obtained in 87% yield by heating equimolecular amounts of I and phenyl isothiocyanate in ethanol. UV spectrum (in ethanol, c 10^{-5} M), λ_{max}, nm, (log ε): 272, 345 (4.01; 4.12). Found: C 59.5; 60.0; N 7.6; 7.8%. $C_{18}H_{20}N_2O_2S_2$. Calculated: C 60.0; N 7.7%.

3-Phenylcyclohexeno[1',2' : 2,3]thieno[4,5-e]-1H-pyrimidin-4-one-2-thione (III). A mixture of 3.6 g (0.01 mole) of II in 30 ml of 2 N sodium hydroxide was heated for 3 h, after which the solution was acidified with concentrated CH_3COOH, and the precipitate was crystallized from dioxane to give 2.8 g (90%) of a product with mp > 250°. UV spectrum (in ethanol, c 10^{-5} M), λ_{max}, nm (log ε): 287, 340 (4.09, 4.20). Found: C 60.9; 61.2; N 8.9; 8.9%. $C_{16}H_{14}N_2OS_2$. Calculated: C 61.1; N 8.9%.

1-Cyanoethyl-3-phenylcyclohexeno[1',2' : 2,3]thieno[4,5-e]pyrimidin-4-one-2-thione (IV). A mixture of 3.15 g (0.01 mole) of III, 5.3 g (0.1 mole) of acrylonitrile, and 2 g of triethylamine in ethanol was refluxed for 2 h. The solution was then poured over ice, and the precipitate was crystallized from ethanol to give 3.3 g (88%) of a product with mp 180-182°. IR spectrum: 1700 (C = O), 1230 (C = S), 2260 (C ≡ N) cm^{-1}. Found: C 61.9; 61.8; N 11.5; 11.4%. $C_{19}H_{17}N_3OS_2$. Calculated: C 62.1; N 11.4%.

Cyclohexeno[1',2' : 2,3]thieno[4,5-e]-1,3H-pyrimidin-4-one-2-thione (V). A mixture of 8.8 g (39 mmole) of I, 14.1 g (185 mmole) of ammonium thiocyanate, 10 ml of water, and 3 ml of concentrated HCl was heated at 60-80° for 3 h and at 110-120° for 2 h. The precipitate was crystallized from dioxane to

Uzhgorod State University. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 567-568, April, 1973. Original article submitted June 13, 1972.

give 5.6 g (60%) of a product with mp 230-232°. UV spectrum (in ethanol, c 10^{-5} M), λ_{max}, nm (log ε): 290, 330, (3.97, 4.14). Found: C 50.3; 50.5%. $C_{10}H_{10}N_2OS_2$. Calculated: C 50.4%.

LITERATURE CITED

1. I. V. Smolanka, A. A. Dobosh, and S. M. Khripak, Ukr. Khim. Zh., 39 (1973).
2. S. M. Khripak, A. A. Dobosh, I. V. Smolanka, and A. S. Mikitchin, Khim. Geterotsikl. Soedin., 2 (1973).
3. K. Gewald, Z. Chem., 2, 305 (1962); Chem. Abstr., 58, 6770 (1963).