In the reaction of 1-ethoxycarbonyl-2-methylthio-1,4,5,6-tetrahydropyrimidine with thiosemicarbazide, 2-aminothiocarbonyl-3-oxo-2,3,5,6,7,8-hexahydro-sym-triazolo[4,3-a]pyrimidine is formed, which as a result of the successive action of methyl iodide, K₂CO₃ solution, and cyclic amines, converts into 2,3,5,6,7,8-hexahydro-8-oxo-sym-triazolo[4,3-a]pyrimidine.

In continuation of the investigations carried out in [2] on the synthesis of new biologically active derivatives of guanidine, several transformations were carried out in order to obtain the derivatives of 2-guanidyl-3-oxo-sym-triazolo[4,3-a]pyrimidine.

As starting compounds, 2-methylthiol-ethoxycarbonyl-1,4,5,6-tetrahydropyrimidine (I) [3] and thiosemicarbazide were used. We might expect that as a result of the reaction, two isomeric compounds, derivatives of pyrimido[2,3-c][1,2,4,6]tetrazepine (II) or sym-triazolo[4,3-a]pyrimidine (III), would be formed.

Among structures II and III the choice was made in favor of III according to the PMR spectrum, in which three one-proton signlets at 7.5, 8.9, and 9.27 ppm were observed in the low field. According to the data already obtained [1], the signal at 7.5 ppm can be assigned to the amidine grouping proton. The position of this proton in the pyrimidine ring is indicated by the presence of a signal of the 7-CH₂ methylene group protons in the spectrum, in the form of a multiplet, which converts into a triplet when heavy water is added (the amidine proton also disappears). The signals at 8.9 and 9.27 ppm may correspond to either

For Communication 3, see [1].
the protons bound to the $N(1)$ and $N(9)$ nitrogen atoms in the structure II, or to the protons of the CS-NH$_2$ group in structure III, which can be explained by a restrained rotation of the thioamide group around the C-N bond, caused by the conjugation of the p-electrons of the exocyclic nitrogen atom with the C=S group [4]. In the reaction of compound (I) with thiosemicarbazide, only compound III is formed, as indicated by the separation of compound IV (previously obtained by the reaction of compound I with hydrazine) in a high yield. Compound IV can be formed only from compound III (but not from II) as a result of splitting of the $N(2)$-C=S bond.

The following stages of the investigation are represented by the scheme

The structure of compound V was confirmed by an alternative synthesis from compound I and thiosemicarbazide hydroiodide [5]. In the PMR spectrum of compound V, there is a singlet of the NH$_2$-N$_2$ group proton at 7.9 ppm, a broadened signal at 8.73-10.12 ppm, characteristic of an amine salt, and a signal of 7-CH$_2$ methylene group protons in the form of a triplet. In the IR spectra of salt V and the starting compound III, the absorption band of the amide grouping CO-N appears at 1730 cm$^{-1}$. These data indicate that the cation of the ammonium salt V formed does not include the $N(4)$ atom in the conjugated system.

In the PMR spectrum of base VI, there are two one-proton singlets at 7.3 and 9.1 ppm, characteristic of the NH-C=N and C=NH group protons.

To obtain the guanidine derivatives, compound VI was reacted with cyclic amines (piperidine, N-methylpiperazine, and N-phenylpiperazine) at 20°C in absolute ethanol. However, instead of the expected guanidine derivatives, compound IV was isolated from the reaction mixture in a high yield.

The data indicate a high lability of the $N(2)$-C=S bond in the sym-triazolo[4,3-a]-pyrimidine system.

**EXPERIMENTAL**

The IR spectra were run on a Unicam SP-200G spectrophotometer in KBr tablets, and the PMR spectra of a Varian spectrometer (60 Hz) in DMSO-$d_6$, using TMS as internal standard.

2-Aminocarbonyl-3-oxo-2,3,5,6,7,8-hexahydro-sym-triazolo-[4,3-a]-pyrimidine (III). A mixture of 2 g (0.01 mole) of compound I and 0.91 g (0.01 mole) of thiosemicarbazide in 10 ml of dry pyridine was boiled for 15 min. The solvent was distilled in vacuo, and 10 ml of ether and 10 ml of acetone were added to the residue, and the precipitate obtained was filtered. Yield, 1.72 g (91%), mp 223-225°C (from ethanol). IR spectrum: 3310, 3220, 1590, 1528 (NH), 1730 (CO), 1400 cm$^{-1}$ (NCS). PMR spectrum: 1.75-2.22 (2H, m, CH$_2$-CH$_2$-CH$_2$); 3.04-3.45 (2H, m, NH$_2$-CH$_2$-CH$_2$); after the addition of D$_2$O, a triplet); 3.49-3.82 (2H, t, N-CO-CH$_2$-CH$_2$); 7.5 (1H, s, NH-C=N); 8.9 and 9.27 ppm (s.s, 2H, CS-NH$_2$). Found: C 36.1; H 4.8; N 35.2. Calculated: C 36.2; H 4.5; N 35.1%.

2-Methylthioimin-3-oxo-2,3,5,6,7,8-hexahydro-sym-triazolo-[4,3-a]-pyrimidine Hydrochloride (V). A mixture of 1.99 g (0.10 mole) of compound III and 1.56 g (0.11 mole) of methyl iodide was boiled in 20 ml of absolute ethanol for 1 h. The solvent was removed in vacuo, and the residue after the removal of ether extracts was ground with ether (2 x 10 ml), and washed with ether. Yield, 2.7 g (79.2%), mp 191-193°C (ethanol-ether). IR spectrum: 3340, 3300, 1620, 1520 (NH), 2860-3160 (NH), 1730 (CO), 1660 cm$^{-1}$ (CN). PMR spectrum: 1.7-2.4 (2H, m, CH$_2$-CH$_2$-CH$_2$); 2.85 (3H, s, SCH$_3$); 3.16-3.57 (2H, t, N-CO-CH$_2$-CH$_2$); 3.6-3.8 (2H, t, N-CO-CH$_2$-CH$_2$); 7.9 (1H, s, N=C-NH-CH$_2$); 8.62-10.00 ppm (2H, br.s, NH). Found: C 24.6;