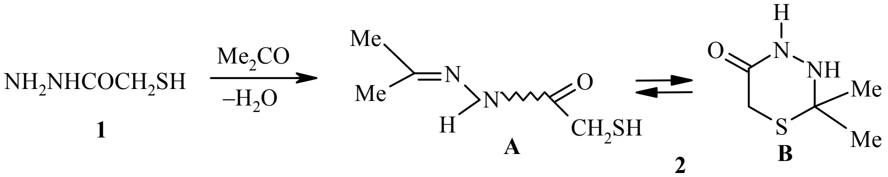
Chemistry of Heterocyclic Compounds, Vol. 37, No. 10, 2001

RING-CHAIN TAUTOMERISM OF ACETONE MERCAPTO-ACETYLHYDRAZONE

A. Yu. Ershov[1] and N. V. Koshmina[2]

Keywords: acetone mercaptoacetylhydrazone, 1,3,4-thiadiazines, ring-chain tautomerism.

The products of the reaction of acetone and hydrazides of lactic and α-aminopropionic acids have linear hydrazone structure [1, 2]. In contrast, previously unreported acetone mercaptoacetylhydrazone obtained upon the brief reaction of equimolar amounts of the hydrazide of thioglycolic acid (**1**) and acetone in water has 1,3,4-thiadiazine structure **2B** in the crystal state. This conclusion was indicated by the ^{13C}H NMR spectrum taken in the solid phase, which shows a typical signal for sp^3-hybrid $C_{(2)}$ at 70 ppm.



A ring-chain tautomeric equilibrium between thiadiazine form **B** and hydrazone form **A** is found in solutions of **2**. Hydrazone form **A** is characterized by downfield shift of the methyl group signals in the ^{1}H NMR spectrum and finding of a signal at 150 ppm for C=N in the ^{13}C NMR spectrum. In addition to the effect of ring-chain tautomerism, doubling of the individual signals is found for hydrazone form **A** in the ^{1}H and ^{13}C NMR spectra due to hindered amide rotation of the mercaptoacetyl group relative to the C–N bond. The observed coexistence of the hydrazone and 1,3,4-thiadiazine forms in solution suggests a means for predicting more complex variants of tautomeric systems [3, 4] containing the mercaptoacetylhydrazone fragment with the involvement of additional cyclic forms in the equilibrium.

2,2-Dimethyl-2,3,5,6-tetrahydro-1,3,4-thiadiazin-5(4H)-one (2) was obtained in 75% yield; mp 69-71°C (hexane). ^{1}H NMR spectrum (pyridine-d_5), form **A** (major conformer, 40%), δ, ppm: 1.82 (s, CH_3); 2.92 (br. s, SH); 3.84 (s, CH_2); 10.35 (br. s, NH); form **A** (minor conformer, 15%): 1.97 (s, CH_3); 3.61 (s, CH_2); form **B** (45%): 1.68 (s, $2CH_3$); 3.70 (s, 6-H); 6.55 (br. s, NH); 10.81 (br. s, NH). ^{13}C NMR spectrum (solid phase), δ, ppm: 30.3 ($2CH_3$ and $C_{(6)}$), 67.9 ($C_{(2)}$), 172.0 ($C_{(5)}$). ^{13}C NMR spectrum (DMSO-d_6): form **A** (major conformer): 18.2 (CH_3), 25.5 (CH_2), 152.2 (C=N), 167.2 (C=O); form **A** (minor conformer): 17.8 (CH_3), 26.8 (CH_2), 157.2 (C=N), 172.4 (C=O); form **B**: 29.4 ($C_{(6)}$), 30.5 ($2CH_3$), 69.1 ($C_{(2)}$), 173.9 ($C_{(5)}$). Found, %: C 41.13; H 6.94; N 19.09. $C_5H_{10}N_2OS$. Calculated, %: C 41.07; H 6.89; N 19.16. The ^{1}H and ^{13}C NMR spectra were taken on Bruker CXP-100, AC-200, and AM-500 spectrometers.

---

[1] Institute of High-Molecular-Weight Compounds, Russian Academy of Sciences, 199004 St. Petersburg, Russia; e-mail: ershov@hq.macro.ru. [2] St. Petersburg State University, 198904 St. Petersburg, Russia. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1431-1432, October, 2001. Original article submitted August 27, 2001.

REFERENCES

1. A. A. Potekhin and V. M. Karel'skii, *Zh. Org. Khim.*, **7**, 2100 (1971).
2. P. S. Lobanov, A. N. Poltorak, and A. A. Potekhin, *Zh. Org. Khim.*, **14**, 1086 (1978).
3. A. Yu. Ershov and A. V. Dobrodumov, *Khim. Geterotsikl. Soedin.*, 825 (2000).
4. A. Yu. Ershov, *Khim. Geterotsikl. Soedin.*, in print.