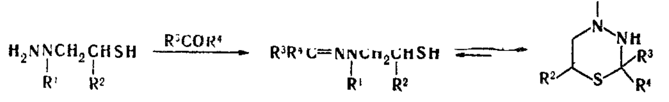
STRUCTURE OF THE PRODUCTS OF CONDENSATION OF 1-(1-ALKYLHYDRAZINO)-2-ALKANETHIOLS WITH CARBONYL COMPOUNDS

S. M. Shevchenko, T. Ya. Vakhitov,
and A. A. Potekhin

UDC 547.879:542.953

We have observed that the products of condensation of hydrazinothiols I-III with aliphatic carbonyl compounds exist in solution primarily, if not entirely, in the form of ring tautomers IVB-VIIIB.



I-III IV A-IX A IV B-IX B

IV R^1=Et, R^2=R^3=Me, R^4=H; V R^1=*i*-Pr, R^2=R^3=H, R^4=Me; VI R^1=*i*-Pr, R^2=H, R^3=R^4=Me; VII R^1=*n*-Pr, R^2=R^3=H, R^4=Me; VIII R^1=*n*-Pr, R^2=H, R^3=Me, R^4=*t*-Bu; IX R^1=Et, R^2=Me, R^3=H, R^4=*p*-ClC_6H_4

The chemical shifts of the substituents of the IVB ring [bp 77-78°C (12 mm) and n_D^{20} 1.4950] in the 2 and 6 positions (δ 1.27 and 1.03 ppm, respectively, in pyridine) and the of ring protons [4.36 (2-H_a), 1.57 (5-H_a), 2.93 (5-H_e), and 3.19 ppm (6-H_a); J_{5a6a} = 10.5, J_{5e6a} = 3.1, and J_{5a5e} = −11.7 Hz] indicate a diequatorial cis orientation of the methyl groups; however, the presence of a low-intensity doublet at 1.34 ppm makes it possible to assume the presence also of a small amount of the trans isomer. The R factors, which correspond to an N—C—C—S torsion angle of 59-61°, were found from an analysis of the portion of the spectrum corresponding to the methylene protons of perhydrothiadiazines V, VII, and VIII [for example, for a solution of the latter in pyridine, δ 1.94 (5-H_a), 2.53 (6-H_e), 2.86 (5-H_e), and 3.29 ppm (6-H_a); J_{5a5e} = −11.9, J_{5a6a} = 11.9, J_{5a6e} = 2.7, J_{5e6a} = 3.4, J_{5e6e} = 3.0, and J_{6a6e} = −13.0 Hz]. Thus the perhydrooxadiazine ring is characterized by somewhat greater puckered character than the perhydrooxadiazine ring [1]. In the case of VI a multiplet of methylene protons of the A_2B_2 type at 2.5-3.0 ppm and a singlet of both 2-Me groups at 1.43 ppm (in CCl_4) are observed in the spectrum because of rapid interconversion of two equivalent chair conformations.

In contrast to the oxygen analogs, which exist in the form of tautomeric mixtures with the corresponding hydrazones (see [2] and preceding communications of this series), ring—chain tautomerism is observed only in the case of pinacolone derivative VIII [bp 101-102°C (6 mm); the n_D^{20} value changes from 1.4791 immediately after distillation to 1.4920 for the equilibrium mixture]. Singlets of methyl and tert-butyl groups of the ring (δ 1.56 and 1.03 ppm, in C_2Cl_4) and acyclic forms (1.91 and 1.10 ppm) are observed in its PMR spectra. The VIIIA:VIIIB ratio depends only slightly on the polarity of the solvent and for example, is ∿1:6 at 30°C for a 20% solution in C_2Cl_4 and 1:1 at 90°C.

It has been pointed out that the reaction of 1-(1-methylhydrazino)-2-propanethiol with benzaldehyde and 3-formylpyridine leads, respectively, to the hydrazone and perhydrothiadiazine [3, 4]. We demonstrated the existence of IXA ⇌ IXB tautomerism in the case of p-chlorobenzylidene derivative IX [bp 135-136°C (1 mm); the n_D^{20} value changes from 1.5939 immediately after distillation to 1.5774 for the equilibrium mixture]. According to the PMR spectrum (of a 20% solution in C_2Cl_4 at 30°C), the equilibrium mixture consists of cis isomer IXB (5.23 ppm, 2-H), trans isomer IXB (5.37 ppm, 2-H), and acyclic tautomer IXA (7.12 ppm, CH=N) in a ratio of 4:1:2. The presence in the products of condensation of IV and IX of trans isomers of the cyclic forms, which were not observed for the oxygen analogs [2], is probably due to the greater length of the C—S bond as compared with the length of the C—O bond, which leads to a decrease in the conformational energies of the substituents in the 2 and 6 positions of the ring.

A. A. Zhdanov Leningrad State University, Leningrad 199164. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1427-1428, October, 1978. Original article submitted February 14, 1978.

0009-3122/78/1410-1165$07.50

All of the compounds obtained have satisfactory analytical characteristics. The structures are also confirmed by the IR spectra.

LITERATURE CITED

1. A. A. Potekhin, in: Problems in Stereochemistry [in Russian], No. 4, Naukova Dumka (1974), p. 12.
2. A. A. Potekhin and E. A. Bogan'kova, Khim. Geterotsikl. Soedin., No. 11, 1461 (1973).
3. D. L. Trepanier and P. E. Krieger, J. Heterocycl. Chem., 4, 254 (1967).
4. D. L. Trepanier, P. E. Krieger, J. H. Mennear, and J. N. Eble, J. Med. Chem., 10, 1085 (1967).

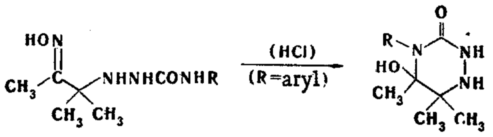
SYNTHESIS OF 5-HYDROXY-4-ARYL-5,6,6-TRIMETHYLPERHYDRO-1,2,4-TRIAZIN-3-ONES

A. F. Rukasov, Yu. G. Putsykin,
Yu. A. Kondrat'ev, V. P. Tashchi,
Yu. A. Baskakov, and E. A. Mertvetsov

UDC 547.873.07

We have synthesized 5-hydroxy-4-aryl-5,6,6-trimethylperhydro-1,2,4-triazin-3-ones (I) (R = 3,4-$Cl_2C_6H_3$, mp 175-176°C; R = 4-ClC_6H_4, mp 120-121°C; R = 2-ClC_6H_4, mp 117-119°C; R = 3-ClC_6H_4, mp 153-153°C [sic]) by treatment of the corresponding N_1-(3-oximino-2-methyl-2-butyl)semicarbazides (II) with a solution of HCl in ethanol with subsequent neutralization of the reaction mixture and isolation of I by the usual methods.

The starting II were obtained by reaction of N-(3-oximino-2-methyl-2-butyl)hydrazine with aryl isocyanates.



II I

The resutls of elementary analysis for C, H, N, and Cl of I were in agreement with the calculated values.

Bands of carbonyl absorption at 1685-1710 cm^{-1} and 1525-1530 cm^{-1}, which are characteristic for the cyclic semicarbazide fragment of the molecule, are observed in the IR spectra of KBr pellets of these compounds. The PMR spectra of I in solutions in perdeuterodimethylformamide with tetramethylsilane as the internal standard contain the singlet of the hydrogen atoms of geminal methyl groups at 1.21-1.28 ppm, a singlet of 5-CH_3 protons at 2.18-2.23 ppm, two singlets of two NH protons at 6.84-7.54 and 8.90-8.98 ppm, a singlet of an OH proton at 4.14-4.93 ppm, and, finally, a multiplet of hydrogen atoms of an aromatic ring at 6.90-8.46 ppm.

All-Union Scientific-Research Institute of Chemical Agents for the Protection of Plants, Moscow 109088. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, p. 1428, October, 1978. Original article submitted April 11, 1978.

0009-3122/78/1410-1166$07.50