Brief Communications

Reaction of thiazolidinethiones with hydrazine hydrate

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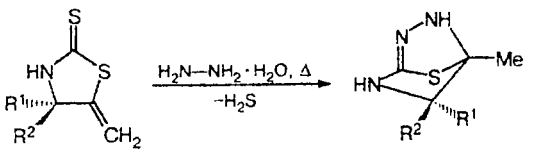
Thiazolidinethiones react with hydrazine hydrate to give bicyclic compounds with a bridge sulfur atom. The bicyclic structure of the reaction products is confirmed by data from ^{1}H NMR and IR spectroscopy.

Key words: thiazolidinethiones, reaction with hydrazine hydrate; bicyclic 3,6-epithio-1,4,5,6-tetrahydro-1,2,4-triazines, IR spectra, ^{1}H NMR spectra.

It is known[1,2] that reactions of thiazolidinethiones with aromatic amines lead to the corresponding thiazolidines. We found that the interaction of compounds **1a,b** with hydrazine hydrate results in formation of a bicyclic system (products **2a,b**).



1a,b **2a,b**

a: R^1 = Me, R^2 = Et
b: R^1 = R^2 = Et

This direction of the reaction is evidenced by ^{1}H NMR and IR spectral data. Absorption bands of the stretching vibrations of the double C=C bond (875 cm^{-1}) and absorption bands at 1205 cm^{-1} corresponding to the stretching vibrations of the C=S bond of the initial thiazolidinethiones **1a,b** are absent in the IR spectra of reaction products. An absorption band was found at 1575 cm^{-1}, which was attributed to the stretching vibrations of the double N=C bond.

The signals of the protons of the methylene group in the range of 4.92—5.04, which are observed in the case of the initial thiazolidinethiones **1a,b**, are absent in the ^{1}H NMR spectra of reaction products **2a,b**, but a signal at δ 1.7 (3 H) attributed to the C—Me group is present. The signals of two protons of the NH groups at δ 8.3 and 10.2 are also observed in the ^{1}H NMR spectra of reaction products, which corresponds to the bicyclic structure of compounds **2a,b**.

Experimental

The synthesis of bicyclic compounds 2a,b (general procedure). A 50% solution of hydrazine hydrate (0.01 mol) was added with stirring to a solution of compound **1a** (1.73 g, 0.01 mol) in 10 mL of dioxane. The reaction mixture was refluxed for 5—6 h until the hydrogen sulfide odor disappeared. The product was precipitated with cold water, and the crystals were filtered off and recrystallized from EtOH.

3,6-Epithio-5-ethyl-5,6-dimethyl-1,4,5,6-tetrahydro-1,2,4-triazine (2a). Yield 1.53 g (90%), m.p. 200 °C. Found (%): C, 49.06; H, 7.54; N, 24.48; S, 18.66. $C_7H_{13}N_3S$. Calculated (%): C, 49.12; H, 7.60; N, 24.56; S, 18.71. ^{1}H NMR (DMSO-d_6), δ: 0.66 (t, 3 H, CH_3, J = 7.0 Hz); 1.12 (s, 3 H, CH_3); 1.44 (m, 2 H, CH_2CH_3); 1.74 (s, 3 H, CH_3); 8.30 (br.s, 1 H, NH); 10.20 (br.s, 1 H, NH).

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3,6-Epithio-5,5-diethyl-6-methyl-1,4,5,6-tetrahydro-1,2,4-triazine (2b). Yield 1.59 g (86%), m.p. 215 °C. Found (%): C, 51.78; H, 8.04; N, 22.62; S, 17.20. $C_8H_{15}N_3S$. Calculated (%): C, 51.89; H, 8.10; N, 22.70; S, 17.29. ^{1}H NMR (DMSO-d_6), δ: 0.68 (t, 6 H, $(CH_3CH_AH_B)_2$, J = 7.0 Hz); 1.42 (m, 4 H, $(CH_3CH_AH_B)_2$); 1.70 (s, 3 H, CH_3); 7.14 (s, 1 H, NH); 10.18 (s, 1 H, NH).

References

1. E. C. Brown, *Chem. Rev.*, 1961, 463.
2. S. M. Ramsh, K. A. V'yunov, A. I. Ginak, and E. G. Sochilin, *Khim. Geterotsikl. Soedin.*, 1972, 775 [*Chem. Heterocycl. Compd.*, 1972 (Engl. Transl.)].

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(4*R*,5*R*)-Bis(*N*,*N*-dimethylaminocarbonyl)-2-chloro-1,3,2-dioxaphospholane: a convenient reagent for control of enantiomeric composition of chiral alcohols by ^{31}P NMR spectroscopy

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The use of enantiomerically pure cyclic chlorophosphite obtained by the reaction of PCl_3 with *N*,*N*,*N*',*N*'-tetramethyldiamide of natural L-(+)-tartaric acid for analysis of the enantiomeric composition of chiral primary and secondary alcohols by ^{31}P NMR spectroscopy is considered.

Key words: chiral alcohols, enantiomeric composition; ^{31}P NMR spectroscopy.

Interest in enantioselective chemical processes is constantly increasing due to the modern requirements of biochemistry, medicine, and technology. Therefore, methods for control of the enantiomeric composition of the final chemical products and reaction mixtures are needed. Polarimetry, chromatography, and NMR spectroscopy are most widely used for this purpose, and each of the methods has both advantages and limitations.[1] Accessibility of standard spectrometers is an advantage of NMR spectroscopy, while the necessity to use expensive enantiomerically pure reagents is its limitation.[2] For the ^{1}H NMR spectroscopy method, additional difficulties appear, which are associated with a narrow interval of change in the chemical shift scale, often making impossible the assignment of signals belonging to different enantiomers. The problem is greatly simplified when NMR on other nuclei is used, in particular, ^{31}P NMR.[3]

As a rule, organophosphorus reagents used for analysis of the enantiomeric composition of chiral alcohols R*OH contain active P—Hal bonds. Reactions with these bonds result in the formation of the R*O—P bonds. These monoadducts with the enantiomeric R*O fragments have different chemical shifts in ^{31}P NMR spectra when the P atom in the starting reagent is either the chiral center or, being achiral, is a part of a chiral molecule. The latter situation is more preferable, because no problems appear related to stoichiometric peculiarities of substitution at the P atom and changes in the initial conformation of the P atom during storage of the reagent. (4*R*,5*R*)-Dialkoxycarbonyl-2-chloro-1,3,2-dioxaphospholanes, cyclic chlorophosphites based on esters of natural tartaric acid, are accessible reagents of this type.[4]

The use of (4*R*,5*R*)-diethoxycarbonyl-2-chloro-1,3,2-dioxaphospholane (**1**) for control of the enantio-

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