2,3,8-Triphenyl-6-[2-(4-oxo-2-thioxo-3-ethylthiazolidin-5-ylidene)ethylidene]thiazolo-[3,4-b][1,2,4]triazine (IXb). A solution of 0.16 g (1 mmole) of 3-ethylrhodanine and 0.62 g (1 mmole) of acetanilidovinyl derivative I in 5 ml of pyridine was refluxed for 5 min, after which the dye was precipitated with 25 ml of water and crystallized from acetic acid–DMF (5:1). The yield was 0.20 g.

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RING-CHAIN TRANSFORMATIONS OF SUBSTITUTED 2-IMINO-1,3-THIAZINOAZOLES

N. D. Abramova, L. V. Andriyankova,
T. V. Kashik, S. M. Ponomareva,
N. N. Chipanina, A. V. Afonin,
and E. S. Domnina

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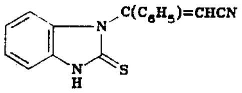
07'792:543.257.1

The ring-chain transformations of substituted 2-imino-1,3-thiazinoazoles in DMSO under the influence of tetraalkylammonium or alkali metal hydroxides were studied by acid–base potentiometric titration and PMR, IR, and UV spectroscopy.

The alkaline opening of the ring of imino-1,3-benzothiazines is known [1, 2]. Irreversible opening of the thiazine ring also occurs in 2-imino-4-phenyl-1,3-thiazino[2,3-b]benzimidazole (I) and leads to the formation of 1-(1-phenyl-2-cyanovinyl)benzimidazole-2-thione (II) [3]. At the same time, the reversible opening of the thiazine ring has been described: When 2,3-dihydro-2-imino-4H-1,3-benzothiazine-4-one is heated in 10% NaOH, the heteroring is opened to give the disodium salt of o-mercaptobenzoylcyanamide [1], while neutralization of a solution of this salt is accompanied by reversible intramolecular cyclization.

In this connection we studied the ring-chain transformations of 2-imino-1,3-thiazinoazoles I and III-V. Thione II was used as a model compound with an open structure [3].



II

Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR, Irkutsk 664033. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 992-994, July, 1988. Original article submitted February 5, 1987; revision submitted September 23, 1987.

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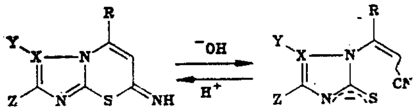
The IR and PMR spectroscopic data provide evidence that 2-imino-1,3-thiazinoazoles I and III-V have a cyclic structure in the crystalline state and in solutions ($CHCl_3$, C_2H_5OH, DMSO) [3-5]. Experiments show that the entire series of investigated compounds, which do not contain functional groups with acidic character, displays clearly expressed acidic properties in the case of titration of them with tetrabutylammonium hydroxide in DMSO: pK_a 12.81 (I), 13.60 (III), 12.90 (IV), 13.30 (V). The manifestation of acidic properties in the case of iminothiazinoazoles I and III-V under the experimental conditions can be explained by opening of the thiazine ring as a result of nucleophilic attack by the hydroxide ion on the carbon atom in the 2 position. Subsequent cleavage of the C—S bond and dehydration lead to the formation of anions with acyclic structures VI-IX. This is in agreement with the data in [2].



I, III–V VI–IX

I, III, VI, VII X=C, Y and Z together form a benzene ring IV, VIII X=C, Y=Z=C_6H_5; V, IX X=N, Z=H; I, VI R=C_6H_5; III—V, VII—IX R=$(CH_3)_2C(OH)$

The dissociation constants indicated above reflect not only ionization of the tetrabutylammonium thiolates but also cleavage of the C—S bond in the starting I and III-V. This explains the lower pK_a value for model compound II (11.35) as compared with iminothiazine I (12.81).

Starting I and III-V in DMSO have a UV absorption band at ~270 nm. A long-wave absorption band appears at 290-300 nm when tetraethylammonium hydroxide is added to these solutions. It should be noted that model compound II is characterized by long-wave absorption at 312 nm, which corresponds to a π—π^* transition in the thioamide group [4]. The similarly constructed acyclic derivative VI has an absorption band at 294 nm.

An intense absorption band of an imino group at 3313 cm^{-1} (in $CHCl_3$) is present in the IR spectra of I and III-V. The absorption band of a nitrile group is a characteristic feature in the IR spectra of derivatives VI-IX. In fact, solutions of I and III-V in DMSO with added tetraalkylammonium or alkali metal (Li, K) hydroxides have an absorption band of a C≡N bond at 2210 cm^{-1}.

2-Imino-1,3-thiazino[2,3-b]benzimidazoles I and III and their derivatives with open structures VI and VII in solution in DMSO with the addition of a twofold excess of tetraethylammonium hydroxide are identified satisfactorily from the positions of the $H_{(3)}$ and $H_{(9)}$ signals in the PMR spectra. Thus for cyclic structure III the chemical shifts of the indicated protons are 6.89 and 8.73 ppm, as compared with 6.24 and 7.45 ppm, respectively, for open form VII; in the investigated solution the acyclic form predominates over the cyclic form by a factor of six. A similar pattern is observed for I.

Acyclic forms VI-IX exist only in the base—DMSO system. Attempts to isolate them from solutions or neutralization of the latter lead to starting compounds I and III-V.

The spectral data and the results of potentiometric titration provide evidence that opening of the 1,3-thiazine ring in iminothiazinoazoles I and III-V under the influence of alkali does not occur in alcohols. Thus the C—S bond in the thiazinoazoles that we investigated is stronger than in benzothiazines [1, 2].

EXPERIMENTAL

The UV spectra of solutions of the compounds (~$3 \cdot 10^{-7}$ M) were recorded with a Specord UV-vis spectrophotometer. The IR spectra of solutions (in DMSO) of the compounds (0.14 M) were obtained with a Specord 75-IR spectrometer; the thickness of the absorbing layer was ~0.1 mm. The PMR spectra of 10% solutions of the compounds in d_6-DMSO were obtained with a Tesla BS-497 spectrometer (100 MHz) with hexamethyldisiloxane (HMDS) as the internal standard.

The acidic ionization constants of I and III-V in DMSO were determined by potentiometric titration at 20°C with a pH-meter-340 using glass (ÉLS-43-07) and silver chloride (ÉVL-1MZ) electrodes. The silver chloride electrode was filled with saturated solutions of LiCl and AgCl in DMSO. The titrant was a 0.1 N solution of tetrabutylammonium hydroxide, which was prepared in benzene—methanol (9:1). The measurements were made at acid concentrations of 0.005 M.

The equivalence points on the titration curves and the half-neutralization potentials (E) were found graphically. Benzoic acid, the acidic ionization constant (pK_a^0) of which in DMSO is 10.9 [7], was used as the standard. The reproducibility of the pK_a values was ±0.1 logarithmic units.

Starting 2-imino-1,3-thiazinoazoles I and III-V were synthesized by the method in [3-5]. The DMSO was purified by vacuum distillation over NaOH.

A 0.08-g (0.3 mmole) sample of 2-imino-4-(1-hydroxy-1-methylethyl)-1,3-thiazino[2,3-b]-benzimidazole (III) was dissolved in 2 ml of DMSO, and 1 ml of a 10% aqueous solution [0.1 g (0.07 mmole)] of tetraethylammonium hydroxide was added.

A 0.1-g (0.4 mmole) sample of III was dissolved in 2-4 ml of DMSO, and 3 ml of a 10% aqueous solution [0.3 g (2 mmoles)] of tetraethylammonium hydroxide was added. The solution heated up and took on a bright-yellow coloration. When the solution was poured into ice water, the yellow coloration vanished, and a white precipitate formed. The precipitate was removed by filtration and washed with water until the wash water was neutral to give 0.08 g of a substance, the melting point and TLC and IR spectral data for which were identical to those for III. Neutralization of the solutions was carried out with 10% HCl.

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POLYFUNCTIONAL MACROHETEROCYCLES.

1. SYNTHESIS OF SULFUR-CONTAINING MACROHETEROCYCLES WITH ENDOCYCLIC AMIDO OR SULFONAMIDO GROUPS

M. G. Voronkov, V. I. Knutov,
and M. K. Butin

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The reaction of 1,8-diamino-, 1,8-bis(2-carbomethoxyethylamino)-, and 1,8-bis(2-phenylethylamino)-3,6-dithiaoctanes and 1,2-bis(2-aminoethylthiomethyl)-4,5-dimethylbenzene with adipic, phthalic, and terephthalic acid dichlorides leads to the corresponding sulfur-containing macrocyclic diamines. Macrocycles that contain endocyclic sulfonamido groups are formed in the reaction of benzene-1,3-disulfonic acid dichloride with hexamethylenediamine and 1,8-bis(2-carbomethoxyethylamino)-3,6-dithiaoctane. The oxidation of 9,10-benzo-8,11-dioxo-7,12-bis(2-carbomethoxyethyl)-1,4-dithia-7,12-diazacyclotetradec-9-ene with 30% hydrogen peroxide was studied.

Polyfunctional macroheterocycles are currently used as complexones and extractants of transition metals [1-4]. Functional groups in the endo- and exocyclic position in the macrocycle molecule intensify its complexing properties and stabilize the formation of a complex [4]. Compounds of this type are used in the synthesis of new types of crown compounds or to

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Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR, Irkutsk 664033.

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