

4',5'-Diiodo, 3',4',5'-Triiodo-, and 3',4',5',6'-Tetraiodobenzo[1',2'-b]-1,4-diazabicyclo[2.2.2]octene (VIII-X). To a solution of 0.64 g (4 mmole) of (I) in 10 ml of 24% oleum was added with stirring 3.0 g (11.8 mmole) of iodine, and the mixture kept at 150°C for 3 h. The preparation of the solution and its neutralization were carried out as described above. Excess iodine was removed by adding 3 g of Na₂S₂O₃·5H₂O, the mixture stirred for 5 min until decolorized, and diluted with 100 ml of water. The iodination products were filtered off, washed with 50 ml of 3% Na₂S₂O₃ solution followed by water, and dried in vacuo to give 1.43 g of a mixture consisting principally of (VIII-X). This was separated by TLC, and the separate components recrystallized from a mixture of chloroform and light petroleum (bp 70-100°C). Compounds (VIII-X) were extracted from the fractions with R_f 0.4-0.5, 0.5-0.6, and 0.8-0.9.

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CYCLOTRIMERIZATION OF THIOCYANIC ACID IN ORGANIC SOLVENTS

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UDC 547.491.8.07'268.5:
542.952

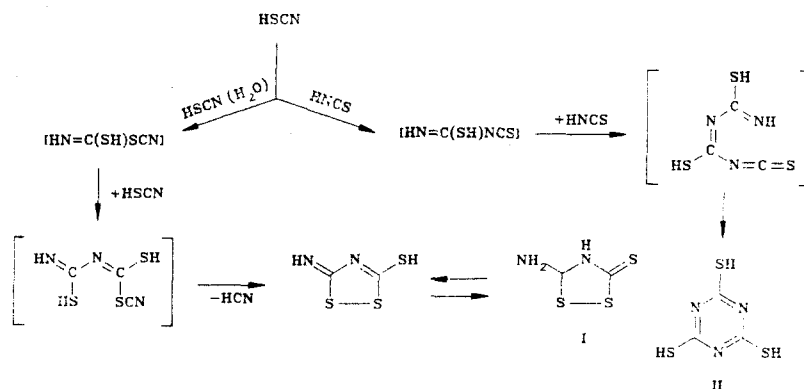
Thiocyanic acid in organic solvents (*i*-PrOH, Bu₂O, AcOH, dioxane) trimerizes to form 1,3,5-trimercapto-sym-triazine.

When thiocyanic acid (TCA) is heated in aqueous medium, the formation of 5-amino-1,2,4-dithiazol-3-thione (I) takes place and hydrogen cyanide is evolved [1]. The purpose of our work was to study the conversion of TCA in organic solvents.

We carried out the reaction in *i*-PrOH, AcOH, Bu₂O, and dioxane. As starting material, we used the pyridinium salt of TCA, which is readily soluble in organic solvents. Heating the solution of pyridinium thiocyanate in organic solvent in the presence of sulfuric acid led to the formation of a yellow powder (II). The UV spectra of products obtained in different solvents were identical and differed from the UV spectrum of compound I. Material II did not melt up to 300°C, dissolved readily in sulfolane and pyridine but poorly in dioxane and benzene. The compound was soluble in aqueous solutions of inorganic acids and bases. The IR spectrum of the compound contained absorption bands characteristic of the triazine ring: 680, 1020, 1400 (C-N), 840, 920, and 1570 (C=N) as well as absorption bands in the 1315 cm⁻¹ region (S-C=N). The molecular mass of the compound, 177, was determined from an analysis of the mass spectrum. The data listed, the PMR spectrum, and also the elementary analysis of the compound indicate that under our experimental conditions, TCA undergoes a cyclotrimerization to form 1,3,5-trimercapto-sym-triazine, II. This conclusion was confirmed by a reverse synthesis [2].

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The formation of compound I from TCA in water and compound II from TCA in organic solvents can be explained on the basis of HSAB principles, according to which soft, weakly solvated reaction centers are more reactive in highly polar solvents, whereas hard, strongly solvated centers become more reactive as the polarity of the medium decreases. In water, the reactive center of TCA at the sulfur atom is more nucleophilic than the reactive center at the nitrogen atom but the reaction center at the nitrogen atom is more nucleophilic in organic solvents of low polarity. Accordingly, the condensation of TCA in water and its cyclotrimerization in organic solvents apparently take place in the following manner:



EXPERIMENTAL

We took the IR spectrum on a UR-20 spectrometer, the UV spectra on an SF-26 instrument, and the PMR spectra on a Tesla BS-487c (80 MHz) instrument. We used C₅D₅N as a solvent (HMDS internal standard). We carried out the mass spectroscopic analysis on an MK 12-01 instrument.

Pyridinium Thiocyanate. We added 75 ml of water to a mixture of 29.4 g (0.3 mole) of potassium thiocyanate and 33.9 g (0.3 mole) of pyridinium chloride and heated it to boiling. The reaction mass was then evaporated down at 20°C. We dissolved the residue in acetone and filtered off the potassium chloride. From the filtrate, we precipitated pyridinium thiocyanate with ether (1:1 by volume). Yield 38.6 g (95%), T_{mp} 100°C.

1,3,5-Trimercapto-sym-triazine (II). Over a period of 8 min we added a mixture of concentrated H₂SO₄ and 5 ml of isopropyl alcohol to a solution of 10 g (0.07 mole) of pyridinium thiocyanate in 15 ml of isopropyl alcohol heated to 90°C. We heated the reaction mixture at this temperature for 1 h 30 min with stirring under reflux. From the cooled reaction mixture we separated the precipitate, washed it with water and dried it. Yield 0.8 g (19%). PMR spectrum: 4.50 ppm (w, SH). Found, %: C 19.8, H 1.3, N 23.6, S 55.1. C₃H₃N₃S₃. Calculated, %: C 19.9, H 1.7, N 23.7, S 54.2. The synthesis was carried out in a similar way in the other solvents. Yields of triazine II were 5% (AcOH), 22% (Bu₂O), and 29% (dioxane).

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