SYNTHESIS OF 1,3-DITHIOLIUM SALTS FROM ACETYLENES AND TETRATHIANIMONIUM DERIVATIVES

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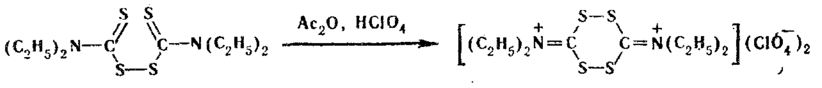
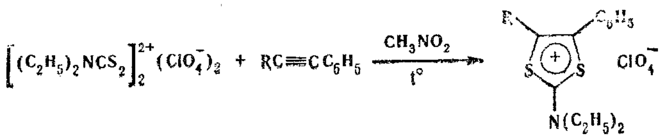
We have found that the addition of perchloric acid to a solution of N,N,N',N'-tetraethylthiuram disulfide (I) in acetic anhydride leads to the formation of the previously undescribed explosive 1,2,4,5-tetrathian-3,6-bis(N,N-diethylimonium) bisperchlorate (II):



I II

Analogs of salt II with different anions are known, but they were obtained by other methods [1-3].

A study of the chemical properties of II led to the development of a new method for the synthesis of 1,3-dithiolium cations (see [4]). It was found that salt II reacts with acetylenes III upon heating in nitromethane to give 1,3-dithiolium perchlorates IV:



II III IV

IV a R=C_6H_5 (mp 197—198°); b R=H (mp 174—178° [5])

The tetrathianimonium cation does not react with acetylenes in acetonitrile even when the mixtures are refluxed. The addition of perchloric acid to the reaction mixture makes it possible to obtain 1,3-dithiolium derivatives IV even in acetonitrile. N,N,N',N'-Tetramethylthiuram disulfide also behaves like disulfide I in these reactions.

The results of elementary analysis of the compounds obtained were in agreement with the calculated values, and the structures were confirmed by IR and PMR spectroscopy.

Bisperchlorate II was prepared as follows. A 0.5-ml (0.006 mole) sample of 70% $HClO_4$ and 2-3 ml of ether were added dropwise successively to a solution of 1 g (0.0034 mole) of disulfide I in 10 ml of Ac_2O, and the precipitate was removed by filtration, washed with ether, transferred in moist form to filter paper, and air dried to give 0.6-0.7 g (∿40%) of product (the product exploded upon heating and impact!).

Perchlorate IVa was prepared as follows. A 0.7-g (1.4 mmole) sample of bisperchlorate II on a filter was dissolved in a mixture of 10 ml of acetonitrile and 0.2 ml (2.4 mmole) of 70% $HClO_4$, 1 g (5.6 mmole) of tolan IIIa was added, and the mixture was refluxed for 2-3 min. It was then cooled, and an oil was liberated by the addition of ether. The upper layer was decanted, ethyl acetate was added to the oil, and the resulting light-colored precipitate was removed by filtration, washed with ethyl acetate and ether, and dried to give 0.5 g (∿50%) of a crude product with mp 197-200°C (from iso-PrOH).

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SYNTHESIS OF PYRROLO[c]- AND PYRROLO[i]PHENANTHRIDINES

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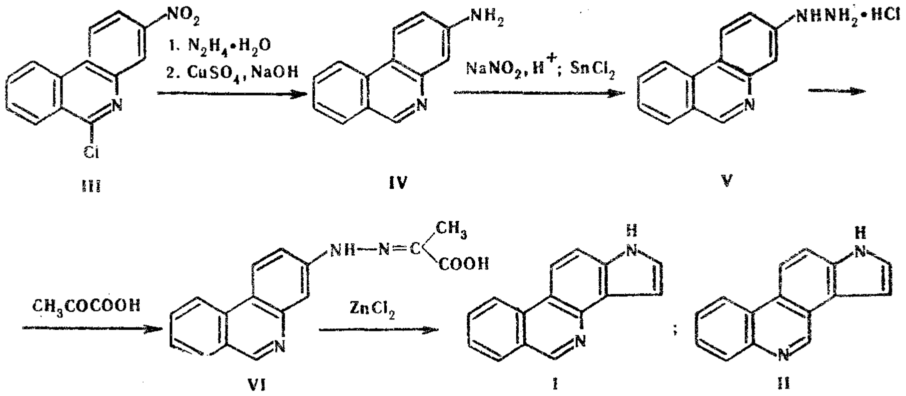
We have synthesized the previously unknown 1H-pyrrolo[2,3-c]- and 1H-pyrrolo[3,2-i]-phenanthridines (I and II), which are analogs of benzophenanthridine alkaloids [1].

The previously undescribed 3-aminophenanthridine (IV), with mp 139-140°C, was synthesized in 40% yield from 3-nitro-6-chlorophenanthridine (III) [2] by the action of hydrazine hydrate with subsequent decomposition of the intermediately formed hydrazine with aqueous $CuSO_4$ solution [3]. The structure of the amine obtained was confirmed by IR, UV, and PMR spectroscopy and mass spectrometry.



Diazotization of amine IV with subsequent reduction yielded 3-phenanthridylhydrazine hydrochloride (V), which gave the corresponding hydrazone VI on treatment with pyruvic acid. Cyclization of hydrazone VI by fusing with anhydrous $ZnCl_2$ [4] led to I, with mp 271-272°C, in 15% yield. PMR spectrum (in DMSO): 11.82 (broad s), 9.84 (s), 8.51 (dd), 8.03 (dd), 7.65 (dd), and 7.36 ppm (m); $J_{AB} \approx 8.8$ Hz. UV spectrum (in alcohol), λ_{max} (log ε): 215 (4.69), 261 (4.79), 337 (4.22), 352 (4.19), and 370 nm (4.20). Mass spectrum: M^+ 218.

Pyrrolophenanthridine II, with mp 267-268°C, was also obtained from a mixture of pyruvic acid 3- and 8-phenanthridylhydrazones, synthesized by a similar method from a mixture of 3-nitro-6-chloro- and 8-nitro-6-chlorophenanthridines (products of the Beckmann rearrangement of stereoisomeric 2-nitrofluorenone oximes [2]), by cyclization with $ZnCl_2$. PMR spectrum (in DMSO): 11.63 (broad s), 9.39 (s), 8.46 (dd), 7.82 (dd), 7.52 (dd), and 7.18 ppm (m); $J_{AB} \approx 8.8$ Hz. UV spectrum (in alcohol), λ_{max} (log ε): 208 (4.56), 220 (4.55), 240 (4.82), 254 (4.69), 275 (4.54), and 345 nm (4.08). Mass spectrum: M^+ 218.

The results of elementary analysis of the compound obtained were in agreement with the calculated values.

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