

SHORT
COMMUNICATIONS

Synthesis of 2,6-Bis(trichloromethyl)-1,2,4,6-thiotriazine-1,1-dioxide Ammonium Salts

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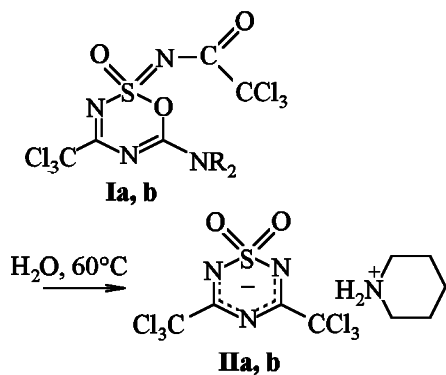
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A new heterocyclic system, 2,4,6-trisubstituted 1,2,3,5-oxathiadiazine 2-oxides (**I**), was recently prepared. Oxides **I** readily react with cyanoamides to form new solvate complexes [3] which on alumina transform into 1,2,4,6-thiatriazines [4].

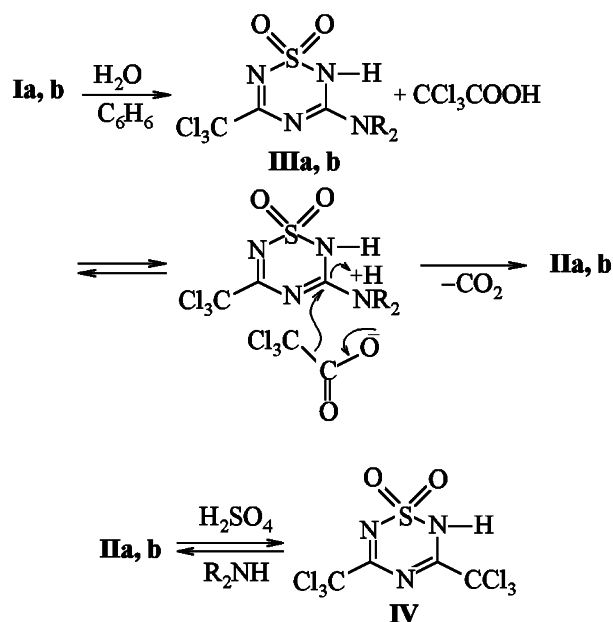
In extension of these studies we established that oxides **I** at heating to 60°C in benzene, toluene, or chloroform with an equimolar amount of water were converted into ammonium salts of 2,6-bis(trichloromethyl)-1,2,4,6-thiatriazine 1,1-dioxide (**IIa, b**).



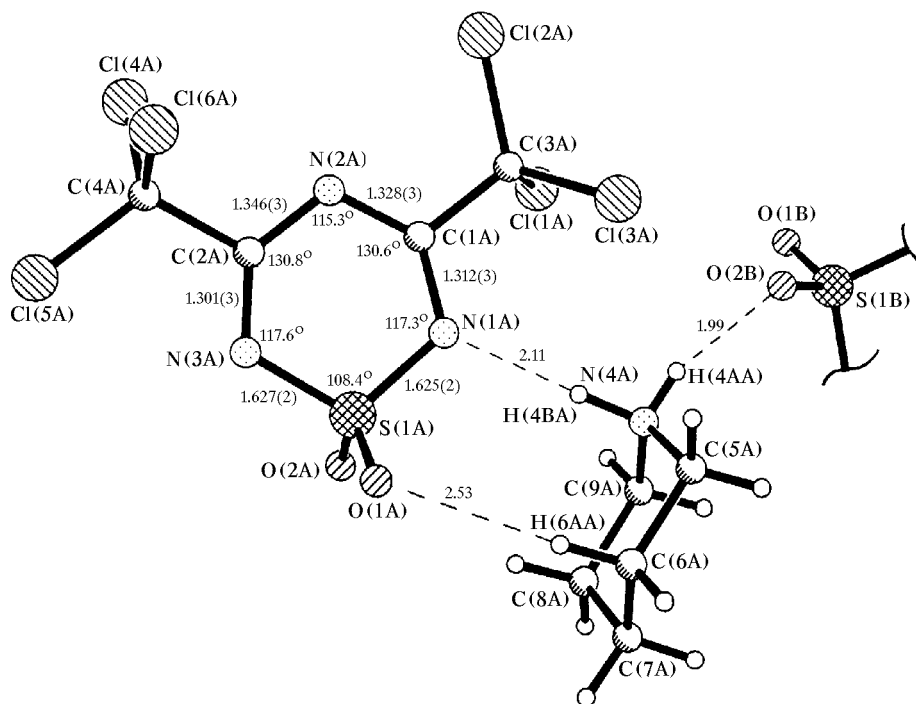
NR₂ = piperidino (**a**); pyrrolidino (**b**).

This process apparently involves a hydrolysis of the trichloroacetamide fragment furnishing in the early stages 1,2,4,6-thiatriazine 1,1-dioxide (**III**) and trichloroacetic acid [4], and later follows uncommon compared to known data [5] substitution of a donor NH₂ group by a strong acceptor CCl₃ group.

By treating salts **IIa, b** with sulfuric acid we obtained 2,6-bis(trichloromethyl)-1,2,4,6-thiatriazine 1,1-dioxide (**IV**) that with piperidine and pyrrolidine gave salts **IIa** and **IIb** respectively.



The composition and structure of salts **IIa, b** and thiatriazine **IV** were confirmed by elemental analysis, IR, ¹H NMR spectra, and chemical reactions. The structure of salt **IIa** was also determined by X-ray diffraction analysis. A fragment of crystal structure of salt **IIa** is shown on the figure. The thiatriazine ring is planar. Atoms C(3) and C(4) deviate from the plane by -0.002 and 0.108 Å respectively. The piperidinium cation is in a *chair* conformation with insignificant deviation of the torsional angles from 60°. Ionic fragments in the crystal are joined into a three-dimensional structure by hydrogen bonds. The bonds N(4A)–H(4BA)···N(1A) [H(4BA)···N(1A) 2.11 Å, N(4A)–H(4BA) 0.97 Å, ∠168.3°] and N(4A)–H(4AA)···O(2B) [O(2B)···H(4AA) 1.99 Å, N(4A)–H(4AA) 0.83 Å, ∠162.0°] according to [6] are strong hydrogen bonds.

A fragment of salt **IIa** crystal structure.

2,6-Bis(trichloromethyl)-1,2,4,6-thiatriazine 1,1-dioxide piperidinium salt (IIa). A solution of 0.40 g (0.84 mmol) of oxide **Ia** in 10 ml of benzene was heated in a sealed ampule for 6 h. The benzene was evaporated, the residue was washed with hexane. We obtained 0.31 g (81%) of salt **IIa**, mp 154°C (dichloromethane-hexane). IR spectrum (CH₂Cl₂), ν , cm⁻¹: 1590 (N-C-N-C-N), 1390, 1170 (SO₂). ¹H NMR spectrum (acetone-*d*₆), δ , ppm: 1.64–1.90 m (6H, CH₂), 3.28–3.40 m [4H, (CH₂)₂N]. Found, %: C 23.41; H 2.52; Cl 46.54; N 12.01; S 7.91. C₉H₁₂Cl₆N₄O₂S. Calculated, %: C 23.86; H 2.67; Cl 46.96; N 12.37; S 7.73.

2,6-Bis(trichloromethyl)-1,2,4,6-thiatriazine 1,1-dioxide pyrrolidinium salt (IIb) was synthesized by the same procedure in 53% yield, mp 130°C (dichloromethane-hexane). IR spectrum (CH₂Cl₂), ν , cm⁻¹: 1590 (N-C-N-C-N), 1390, 1170 (SO₂). Found, %: C 22.23; H 2.35; Cl 48.10; N 12.25; S 7.30. C₈H₁₀Cl₆N₄O₂S. Calculated, %: C 21.89; H 2.30; Cl 48.46; N 12.76; S 7.30.

2,6-Bis(trichloromethyl)-1,2,4,6-thiatriazine 1,1-dioxide (IV). To 0.23 g (0.05 mol) of salt **IIa** was added 2.5 ml of concn. H₂SO₄, and the reagents were thoroughly mixed and then kept for 15 min at 25°C. The precipitate was filtered off, washed on the filter with cold water, dissolved in dichloromethane,

dried, and the solvent was evaporated. The residue was washed with 4 ml of ether to obtain 0.4 g (95%) of dioxide **IV**. Decomposition temperature over 200°C. IR spectrum (mull in mineral oil), ν , cm⁻¹: 1600, 1640 (C=N), 1390, 1170 (SO₂). Found, %: C 13.56; H 0.32; Cl 57.01; N 11.12; S 8.95; neutralization equivalent 365.81. C₄HCl₆N₃O₂S. Calculated, %: C 13.06; H 0.27; Cl 57.82; N 11.42; S 8.70; neutralization equivalent 367.85. On mixing dioxide **IV** with equimolar quantities of piperidine or pyrrolidine in dichloromethane were isolated salts **IIa** and **IIb** respectively.

IR spectra were recorded on spectrophotometer UR-20. ¹H NMR spectra were registered on spectrometer Varian Gemini (300 MHz) at 20°C, internal reference HMDS.

X-ray diffraction analysis was performed on diffractometer SMART 1000 at 100 K (MoK α -radiation, graphite monochromator, ω -scanning, $2\theta \leq 60^\circ$). Crystals of salt **IIa** monoclinic, *a* 8.8742(10), *b* 12.7179(14), *c* 15.4155(17) Å, ρ 98.803(2)^o, *V* 1714.4(3) Å³, *Z* 4, d_{calc} 1.755 g·cm⁻³, space group P2₁/C. Overall number of reflections measured 41 817 (R_{INT} 0.042), therewith 4972 independent reflections with $I > 2\sigma(I)$ were used in solving and refining of the structure. The absorption was accounted for along SADABS software [7]. The structure was solved by

combining the direct method with Fourier analysis of the electron density. All the nonhydrogen atoms were refined in the anisotropic approximation. Except atoms H(4A) and H(4B) at N(4) atom the positions of all hydrogens were calculated from geometrical considerations and were refined in the "rider" model. The positions of atoms H(4A) and H(4B) were found from the difference synthesis and refined in isotropic approximation. The final values of *R*-factors are as follows: *R* 0.064, *R_w* 0.074, *S* 1.3. All calculations were carried out with the use of software package SHELXTL [8].

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