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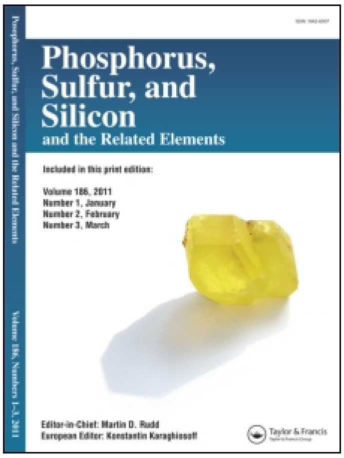

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The Oxidation of Trlthlocyanurlc Acid and Of Its N-and S-Esters

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To cite this Article Tripolt, Robert and Nachbaur, Edgar(1992) 'The Oxidation of Trlthlocyanurlc Acid and Of Its N-and S-Esters', Phosphorus, Sulfur, and Silicon and the Related Elements, 65: 1, 173 — 176

To link to this Article: DOI: 10.1080/10426509208055346

URL: http://dx.doi.org/10.1080/10426509208055346

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Phosphorus, Sulfur, and Silicon, 1992, Vol. 65, pp. 173–176
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THE OXIDATION OF TRITHIOCYANURIC ACID AND OF ITS N- AND S- ESTERS

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Abstract The reaction of trithiocyanuric acid **1** with 3 equivalents of 2-benzenesulfonyl-3-phenyl-oxaziridine affords the highly reactive 1,3,5-triazine-2,4,6-trisulfenic acid **3**, which is trapped by reaction with diazomethane to give the trimethylester of **3**. Additionally the reactions of trithioisocyanurates and trithiocyanurates with meta-chloroperbenzoic acid (mCPBA), oxaziridine, dimethyldioxirane and chlorine are studied.

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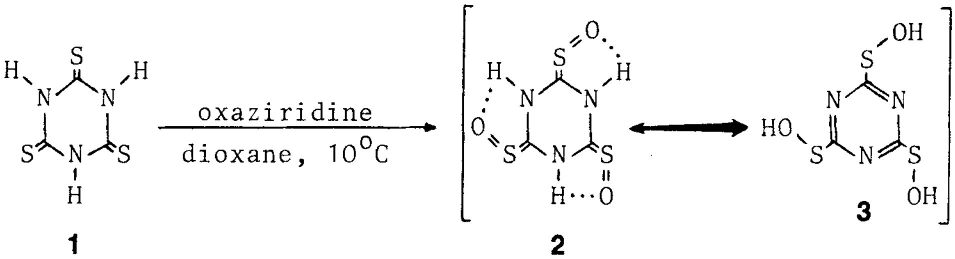
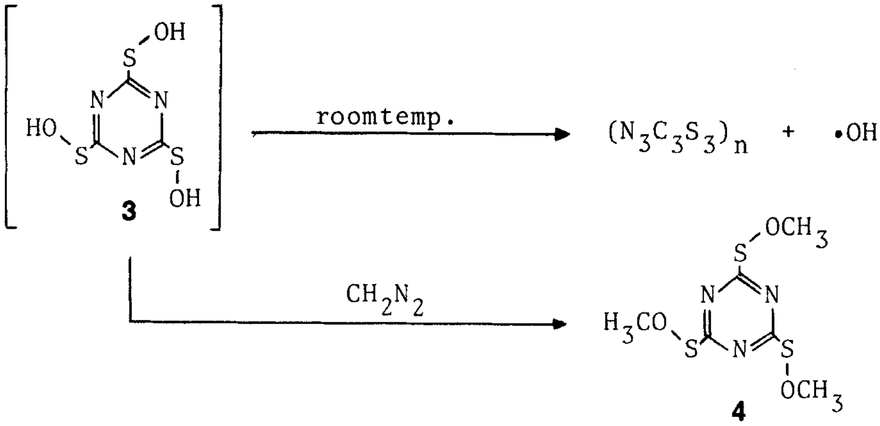
OXIDATION OF TRITHIOCYANURIC ACID 1

Controlled oxidation of **1**, which is thought to be a heteroenethiolizable compound, yields the corresponding trisulfine **2**, which should be stabilized by intramolecular hydrogen bonding. To the contrary, rapid tautomerisation of **2** yielding 1,3,5-triazine-2,4,6-trisulfenic acid **3** was detected by IR-spectroscopic measurements.

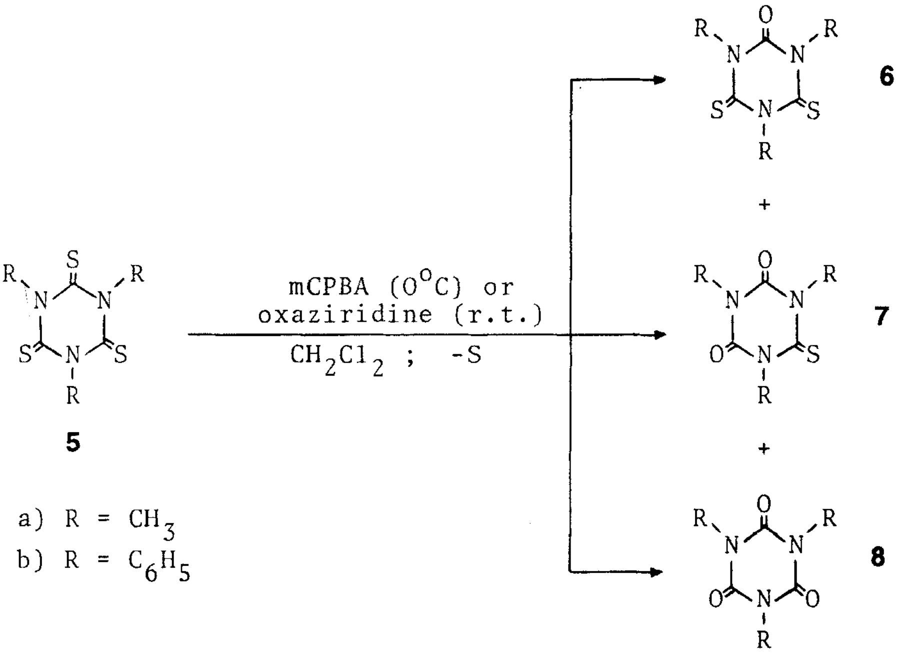


Decomposition of **3** quantitatively affords insoluble polymeric disulfides and ·OH-radicals within a short time. Latter were detected by the method of Nakanishi et al[1]. The formation of H_2O_2 in the reaction solution is not detectable by TLC. The highly reactive trisulfenic acid **3** was trapped by reaction with diazomethane yielding the corresponding trimethylester **4**.



OXIDATION OF TRITHIOISOCYANURATES 5

The oxidation of thiocarbonyl compounds is a well established method for synthesizing sulfines[2]. In the reaction of the N,N',N''-trimethyl- and the N,N',N''-triphenylester of **1** with mCPBA or oxaziridine we detected the formation of the



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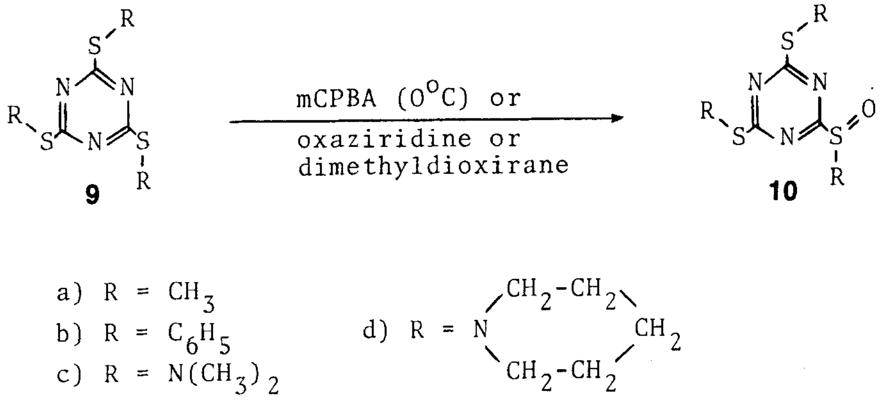
corresponding esters of dithio- **6**, monothio- **7** and cyanuric acid **8** as the only reaction products. These observationes may be explained by formation of intermediate oxathiiranes followed by sulfur extrusion[3].

OXIDATION OF TRITHIOCYANURATES 9

The oxidation of sulfides to sulfoxides and sulfones has been the subject of extensive studies and a number of useful oxidants are now available[4-6]. We wish to report the behaviour of trithiocyanurates in the reaction with different oxidizing agents, which revealed the formation of unexpected products. Oxidation of **9** with one equivalent mCPBA, oxaziridine or dimethyldioxirane produces the corresponding "monosulfoxides" **10**. More than one equivalent of oxidizing agent causes C-S bond cleavage, thereby avoiding the formation of the corresponding "trisulfoxides" and "trisulfones" respectively.



9 **10**

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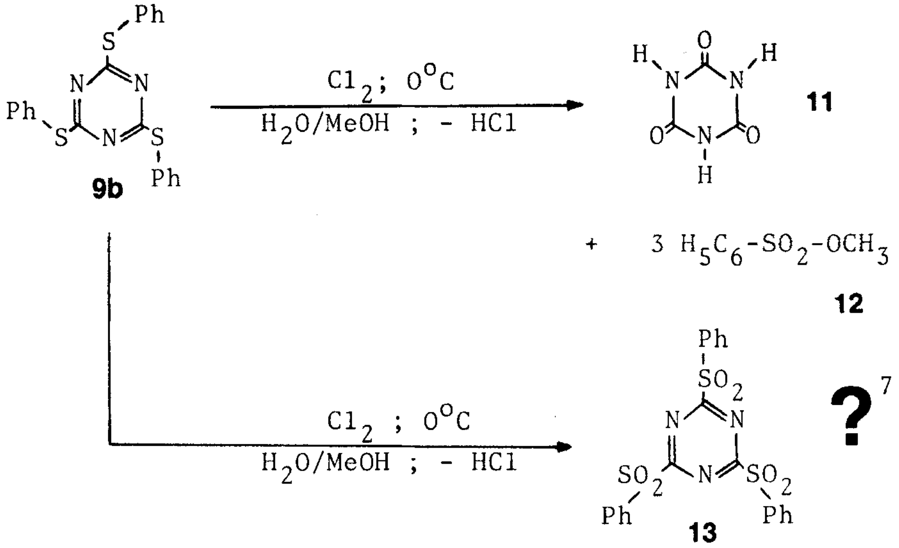
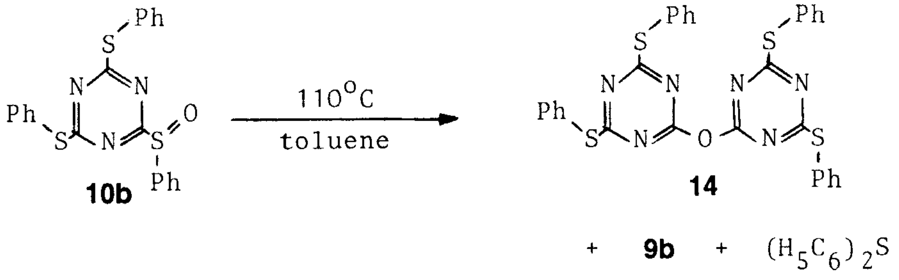
According to this observation and in sharp contrast with literature data[7] the reaction of triphenyltrithiocyanurate **10b** with chlorine in aqueous methanol yields cyanuric acid **11** and methylbenzenesulfonate **12** as the only reaction products and no 2,4,6-tris(phenylsulfonyl)-1,3,5-triazine **13** is formed.

The "monosulfoxides" do not undergo a Meisenheimer rearrangement (sulfoxide ⟶ sulfenate) at temperatures up to 100°C. Thermolysis of **10b** at 110°C results in the formation of 2,2 -oxybis[4,6-bis(phenylthio)-1,3,5-triazine] **14**.





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