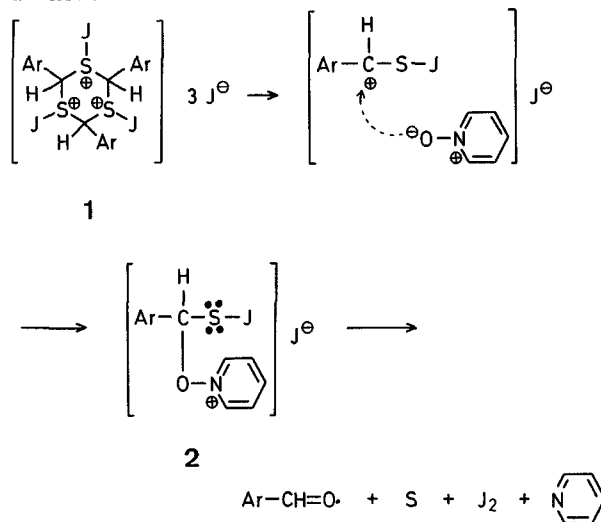


The reactions of the *s*-trithianes probably involve the formation of a sulfonium complex with iodine (1), followed by the rupture of the ring and the nucleophilic addition of oxygen of pyridine *N*-oxide may lead to (2) which ultimately leads to benzaldehyde, sulfur and pyridine. Alternatively pyridine *N*-oxide may attack (1) followed by ring rupture as shown below.



Heterocycles: Part VI: An Oxidative Desulfurisation of *s*-Trithianes with Iodine and Pyridine *N*-Oxide*

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The usefulness of 1,3-dithioacetal group is of wide interest in organic synthesis¹ and numerous methods have become available to achieve its removal under a variety of hydrolytic conditions². Recently we have reported that iodine in dimethyl sulfoxide effects the conversion by oxidative desulfurisation into the corresponding aldehydes or ketones in very good yields³. Now we wish to report a similar oxidative cleavage of triphenyl-*s*-trithiane ring system to the corresponding carbonyl compound by iodine and pyridine *N*-oxide.

Thus in a typical experiment, a mixture of 2,4,6-triphenyl-*s*-trithiane, iodine, and pyridine *N*-oxide in cellosolve was heated to reflux for 8 h and the reaction mixture on working up gave benzaldehyde in 40% yield. Pyridine and sulfur have been obtained as end products. The yield could not be improved by refluxing the reaction mixture for a longer period. Under an identical experimental condition 1,3-dithioacetals could be recovered unchanged.

Following the same procedure a number of substituted triaryl-*s*-trithianes such as *p*-chlorophenyl, anisyl and piperonyl have been oxidatively desulfurised to the corresponding aldehydes (see Table).

Table. Aldehydes from Triaryl-*s*-trithianes

| Ar | Yield (%) of aldehyde | B. p. | (Lit. ⁵ B. p.) |
|--|-----------------------|----------|---------------------------|
| C ₆ H ₅ | 40 | 176–179° | (179.5°) |
| 4-H ₃ CO–C ₆ H ₄ | 37 | 245–247° | (247°) |
| 3,4-(O–CH ₂ –O)–C ₆ H ₃ | 33 | 263° | (263°) |
| 4-Cl–C ₆ H ₄ | 31 | 212–214° | (214°) |

Earlier it has been shown that pyridine *N*-oxide converts alkyl halides to aldehydes⁴.

Oxidative Desulfurization of Triaryl-*s*-trithianes using Pyridine *N*-Oxide and Iodine:

A mixture of triphenyl-*s*-trithiane (3.66 g, 0.01 mol), iodine (3.87 g, 0.03 mol), pyridine *N*-oxide (3.8 g, 0.04 mol) in 2-methoxyethanol (30 ml) was refluxed for 8 h and the dark coloured solution was poured in water. Excess of iodine was destroyed by an aqueous solution of sodium thiosulphate (4 g) in water (15 ml). The colourless solution on extraction by petroleum ether and evaporation of the solvent gave a liquid; yield: 1.3 g, which was distilled at 176–179° and was identified as benzaldehyde. The aqueous filtrate after petroleum ether extraction was extracted with ether (5 × 20 ml). The evaporation of the ethereal extract gave a liquid; yield: 1.7 g, b. p. 115° identified as pyridine.

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