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A NOVEL OXIDATIVE DESULPHURISATION OF s-TRITHIANES AND THIOACETALS WITH IODINE IN DIMETHYLSULPHOXIDE.*

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The usefulness of thioacetal group is of wide interest in organic synthesis[1,2] and numerous methods have become available to achieve its removal under a variety of hydrolytic conditions.[3] Recently we have adopted a simple and convenient method of preparing α-*d*-aromatic aldehydes from trideuterated-triaryl-*s*-trithianes obtained by refluxing triaryl-*s*-trithianes in dioxane with a solution of 20% NaOD in D_2O.[4] We have also found that silver oxide in aqueous methanol smoothly hydrolyses the *s*-trithianes to the corresponding aldehydes or ketones;[5] a method employed independently by Gravel *et al.*[3] for the hydrolysis of thioacetals. We have now found that iodine in dimethylsulphoxide does effect the conversion of *s*-trithianes and thioacetals by a novel oxidative desulphurisation into the corresponding aldehydes or ketones in very good yields.

In a typical experiment, a mixture of 2,4,6-triphenyl-*s*-trithiane (3.66 g., 0.01 mole) and iodine (3.81 g., 0.03 atoms) was dissolved in DMSO (20 ml) and the solution was heated on a steam bath for an hour. During the course of the reaction a volatile fraction, distilling at 35-38°, was collected and characterised as dimethylsulphide (1.4 g). The solution was cooled, diluted with cold water (100 ml) and the free iodine was destroyed by adding a solution of sodium thiosulphate (4 g) in water (15 ml). A pale yellow solid was precipitated out of the solution (0.8 g., m.p. 121-22°) and identified as elemental sulphur. The aqueous solution was extracted with pet.ether. Removal of the solvent gave an oil (3 g., 94%), characterised as benzaldehyde(b.p.; 2,4-DNP).

Adopting the same procedure, a few *s*-trithianes and thioacetal derivatives of ketones have been oxidised to give the corresponding aldehydes or ketones in good yields.

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TABLE: Oxidation of s-trithianes and thioacetals with DMSO and iodine.

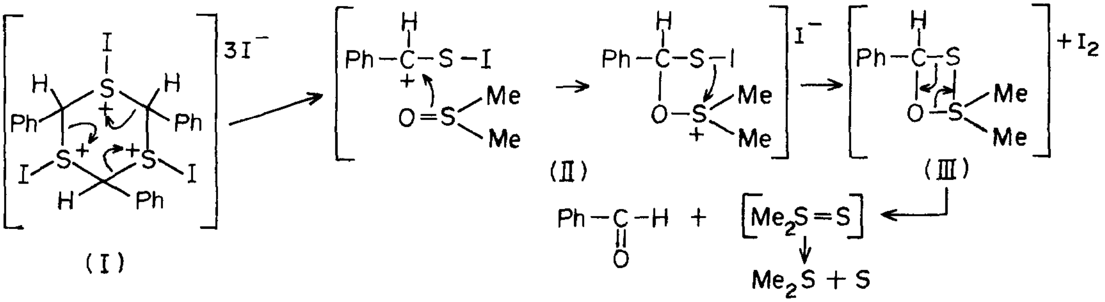
s-Trithianes	Yield* of parent aldehyde or ketone (%)
1. Trithioformaldehyde$(CH_2S)_3$	63+
2. 2,4,6-tris(phenyl)-	94
3. 2,4,6-tris(p-methoxyphenyl)-	79
4. 2,4,6-tris(3,4-methylenedioxy-phenyl)-	83
5. 2,4,6-tris(p-chlorophenyl)-	76
6. 2,4,6-tris(methyl-phenyl)-	87

Thioacetal deriv. of ketones	Yield* of parent ketone (%)
1. Cholestan-3-one	76
2. 4,6-Cholesten-3-one	81
3. Cyclohexanone	84

* Conversions are quantitative, losses are due to working up procedure and purification. All products have been characterised by the melting point or boiling point.

\+ Yield based on 2,4-DNP.

The reaction on s-trithianes probably involves the formation of a sulphonium complex with iodine (I), followed by the rupture of the ring and the nucleophilic addition of dimethylsulfoxide may lead to (II)ǂ, which may result finally in the products isolated through (III); iodine being needed in the reaction in catalytic amounts.



ǂ Alternatively the attack by DMSO may be followed by ring rupture.

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