

Efficient Synthetic Methodology for 1,3-Dithiolane 1-Oxides *via* Singlet Oxidation of 1,3-Dithiolanes†

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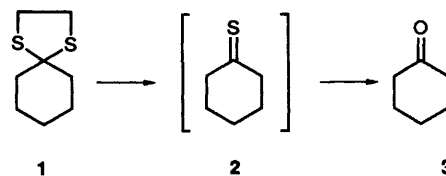
Singlet oxidation of 1,3-dithiolanes furnishes synthetically useful yields of 1,3-dithiolane 1-oxides. However, 2-ethyl-2-phenyl-1,3-dithiolane **13** gave 2-ethyl-4-hydroxy-2-phenyl-1,3-dithiolane **19** as a major product.

1,3-Dithiolane constitutes an important functional group in organic chemistry, but, its photochemistry remains unexplored. Broadly speaking, photolysis of 1,3-dithiolanes, in the absence of oxygen, leads to product(s) derived from initial C–S bond cleavage.^{1,2} Thus, Berchtold *et al.*² have rationalized the formation of various photolysis products from dithiolane **1** *via* thioketone **2** (Scheme 1). Recently, Takahashi *et al.*³ have reported a unique and efficient photodethioketalization of 1,3-dithiolanes in the presence of triplet sensitizers and molecular oxygen, but without suggesting any mechanism. For example, photolysis of **1** and benzophenone in an oxygen atmosphere is shown to give ketone **3** (65%).³ Since singlet oxidation of thioketones, *e.g.* **2**, are known to yield ketones, *e.g.* **3**,^{4,5} we were curious as to whether ¹O₂, generated by the interaction of either triplet sensitizer⁶ or photochemically derived thioketone⁵ with molecular oxygen, accomplishes dethioketalization.

Also, our recent interest in hydroperoxide-type intermediates *e.g.* **22** (Scheme 3),⁷ which could also be obtained by singlet oxidation of dithiolanes, prompted us to examine the reaction of ¹O₂ with 1,3-dithiolanes. As a result, this communication describes a synthetically useful methodology for the preparation of 1,3-dithiolane 1-oxides under neutral and mild conditions and concludes that ¹O₂ is certainly not the species involved during Takahashi dethioketalization.³

Results and Discussion

The various 1,3-dithiolanes (**1**, **4**, **11–13**) and 1,3-dithianes (**7**, **8**, **14**) were prepared according to the literature procedure⁸ and singlet oxidation was carried out, in MeOH, as per the standard procedure, with slight modification (for details see Experimental



Scheme 1.

section). Normally >90% of dithiolane or dithiane was consumed during singlet oxidation, although the reaction was fast in the early stages of irradiation. Identical products were obtained with either Rose Bengal or Methylene Blue as sensitizers, ensuring the involvement of ¹O₂. Although many variations in experimental conditions are possible as far as duration of irradiation, degree of O₂-saturation/agitation, solvent variation, and concentration of substrate and photosensitizer are concerned, the above reaction conditions furnished synthetically useful yields of 1,3-dithiolane 1-oxides and 1,3-dithiane 1-oxides as shown in Scheme 2.‡ The stereoselectivity of oxygenation was governed by steric factors. Thus, the major stereoisomers of compounds **16** and **17** contained oxygen 'syn' to the alkyl group, which could be easily ascertained by ¹H NMR. Interestingly, no di-S-oxides or sulphone was observed during singlet oxidation,⁹ and, surprisingly, no dethioketalization occurred either! Subsequently we have examined the validity of 65% yield of **3** from **1** under reported experimental conditions with a 200 W lamp.³ However, we faced problems in reproducing these results; with repeated trials, a maximum of only 10% dethioketalized product **3** could be observed by GLC.§

Another unusual observation was the isolation of the OH insertion product **19** (50%),‡ besides the 1,3-dithiolane 1-oxide **17** (32%) during the singlet oxidation of 2-ethyl-2-phenyl-1,3-dithiolane **13**. However, such insertion products could not be observed with other substrates, even after repeated trials.

The tentative mechanism for this complex oxygenation process is shown in Scheme 3. Presumably, the formation of dithiolane S-oxides and OH insertion products both could be rationalized *via* the hydroperoxide **22**, which could be formed either *via* a step-wise electron transfer process through a tight

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‡ All 1,3-dithiolane 1-oxides were characterized by satisfactory IR, ¹H NMR and mass spectroscopy. A characteristic feature of the S-oxides was a strong absorption at ν 1050 cm⁻¹ in the IR and complex multiplets between 2.6 and 4.0 in the ¹H NMR for the methylenes in the dithiolane skeleton. Wherever possible, authentic sample of dithiolane S-oxides were prepared by known methods,^{7,15} and superimposability of IR spectra was confirmed. Selected spectral data for both isomers of **19** are as follows: ν_{\max} (film): 3400br/cm⁻¹; δ_{H} (CDCl₃) 0.75–1.00 (3 H, m), 2.3 (3 H, q), 3.0–3.5 (2 H, m), 5.8 (1 H, br s, D₂O exchangeable), 7.2–7.4 (3 H, m) and 7.5–7.7 (2 H, m); δ_{C} (CDCl₃) 11.14 and 12.19 (q), 38.59 and 39.29 (t), 47.09 and 47.62 (t), 86.35 and 86.59 (d), 126.91, 127.60, 127.78, 127.90 and 128.19 (aromatic); m/z : 226 (M⁺, 5%), 197 (40) and 121 (100).

§ Some other side products could be observed by GLC.

