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DIRECT OBSERVATION OF A DIOXETANE FROM THE SINGLET OXYGEN PHOTOOXYGENATION OF A THIOKETENE ACETAL

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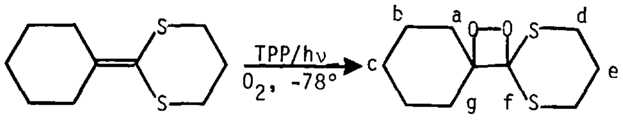
Abstract: A dioxetane from a thioketeneacetal has been characterized at low temperature.

Dioxetanes have been postulated as the initial products of the reaction of singlet oxygen with several sulfur substituted olefins such as thioketene acetals and tetrathioethylenes.[1-7] In all of these studies the intermediacy of the dioxetane has been inferred from secondary products presumably obtained from dioxetane decomposition, but in no case has a sulfur-substituted dioxetane been observed directly. Here we report the first direct spectroscopic observation of a dioxetane obtained from the photooxygenation of a thioketene acetal.

Dioxetane II was obtained by tetraphenylporphine sensitized photooxygenation of 2-cyclohexylidene-1,3-dithiane(I)[8,9] in Freon-11/deuterochloroform at -78°C.



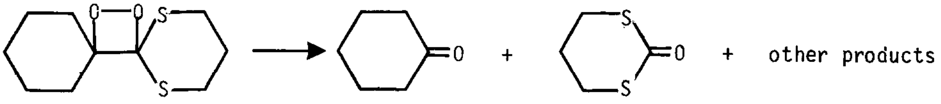
I

II

The ^1H and ^{13}C NMR spectra were obtained at low temperature without allowing the sample to warm[10] and are consistent only with structure II.

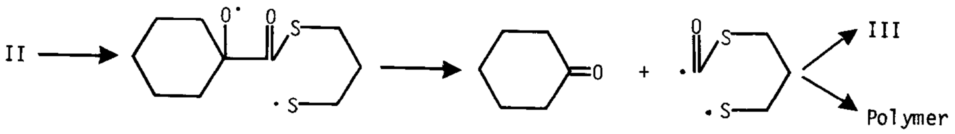
The analysis of the NMR spectra is complicated by dynamic equilibria between various conformers at low temperature. The 200 MHz ^{1}H NMR signals at -58°C and -78°C were poorly resolved multiplets centered at (δ, TMS) 1.2, 1.40, 1.93, 2.35, and 2.82 ppm. The signals were not integrated because of the poor resolution. This spectrum showed dramatic and reversible changes in line shape as the temperature was changed from -78°C to -58°C and back again.[11] The ^{13}C spectrum was more definitive; the signals of the five methylene carbons at -58°C were assigned as follows: (δ, TMS) a, 25.6; b, 24.9; c, 22.4; d, 32.6 (broad); e, 21.0 (broad); f, 109.2; g, 94.2 ppm. For comparison, Adam reports 96.6 and 109.6 ppm for corresponding quarternary carbons in a similar dioxetane.[12] At lower temperatures the signals were split due to conformational effects. Previous studies have shown that the activation energy for chair-chair interconversion of 2,2-dimethyl-1,3-dithiane is 9.8 ± 0.2 kcal/mole while that of 1,1-dimethylcyclohexane is much lower.[13] This high activation barrier is consistent with the broadening observed below -58°C for the carbons of the dithiane ring.

At temperatures higher than -58°C, dioxetane II undergoes decomposition; at -38°C, measured by ^{1}H NMR, the half-life was one hour.



II 100% III, ≤46%

The major decomposition products are cyclohexanone and 2-oxo-1,3-dithiane (III) products of C-C and O-O cleavage of the dioxetane, further confirming the structure of II. Both products are clearly visible in the nmr spectra (^{1}H and ^{13}C) of the decomposition mixture. An authentic sample of III was prepared from phosgene and 1,3-propanethiol.[14] Both products were compared with authentic samples by NMR spectroscopy after purification by GC and prep. TLC.[15] Yields were determined by GC: cyclohexanone was always formed in quantitative yield, whereas the yield of III varied in different runs, the maximum being 46%. Other materials were apparent in the NMR and chromatographs of the decomposition materials. In particular, pure samples of III were not stable to photooxidation under the conditions. An insoluble, non-volatile, poorly characterized material formed in most of the samples. These by-products may stem from two sources: further photooxidation of III, and the well precedented[1-7] C-S cleavage process of sulfur-substituted dioxetanes, which may compete with C-C cleavage of II.



A third possibility is that the dioxetane reacts intermolecularly with the sulfur atom of another dioxetane. (The reaction of dioxetanes with sulfides is well known.)[16,17]

When samples of the dioxetane were decomposed by rapid warming to room temperature in the dark, no luminescence was observed. However, when a small amount of 9,10-Dibromoanthracene (DBA) was added, strong blue luminescence was observed. This observation is consistent with expectations that neither cyclohexanone or III are fluorescent, but that DBA can trap the triplet product by triplet-singlet energy transfer to give the fluorescent ^{1}DBA.[18] The observation of luminescence strongly suggests that C-S cleavage, which would not be expected to lead to luminescent products, is not the sole route for decomposition of II.

After this manuscript was completed, a paper appeared reporting the detection of two sulfur-substituted dioxetanes from the adamantylidene series.[12] These compounds, as might be expected from the properties of other adamantylidene dioxetanes,[19] are considerably more stable than Compound II.

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15. The GC column used was 6' X 1/8", 10% OV-101 on 100-120 mesh Chromosorb W. The nitrogen flow rate was 30 ml/min, and a temperature program with a 5°C/min rise from 150°C to 200°C was employed.
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