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THE REACTION OF SINGLET OXYGEN WITH A SIMPLE THIOPHENE

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Current interest in the reactions of singlet oxygen with heterocyclic systems prompts us to describe some of our own efforts in this area.[1] The marked reactivity of singlet oxygen with *cis*-dienes is well documented,[2] and this behavior suggested that it might be possible to obtain a reaction between singlet oxygen and simple thiophenes. This supposition has proven correct for we have found that photogenerated singlet oxygen undergoes an interesting and facile reaction with 2,5-dimethylthiophene (1).[3]

Irradiation (4 hrs) of chloroform solutions of 1 (0.013 M) with 520 nm light absorbed only by the sensitizer methylene blue gave rise to the *cis*-sulfine 2 (56% yield) and the *trans*-diketone 3 (28% yield).[4] The same reaction carried out in methanol gave sulfine 2 in 70% yield along with the diketone 3 in 2% yield. Unreacted thiophene was the remainder of the reaction mixture in these experiments and the mass balance for both reactions was greater than 95%.

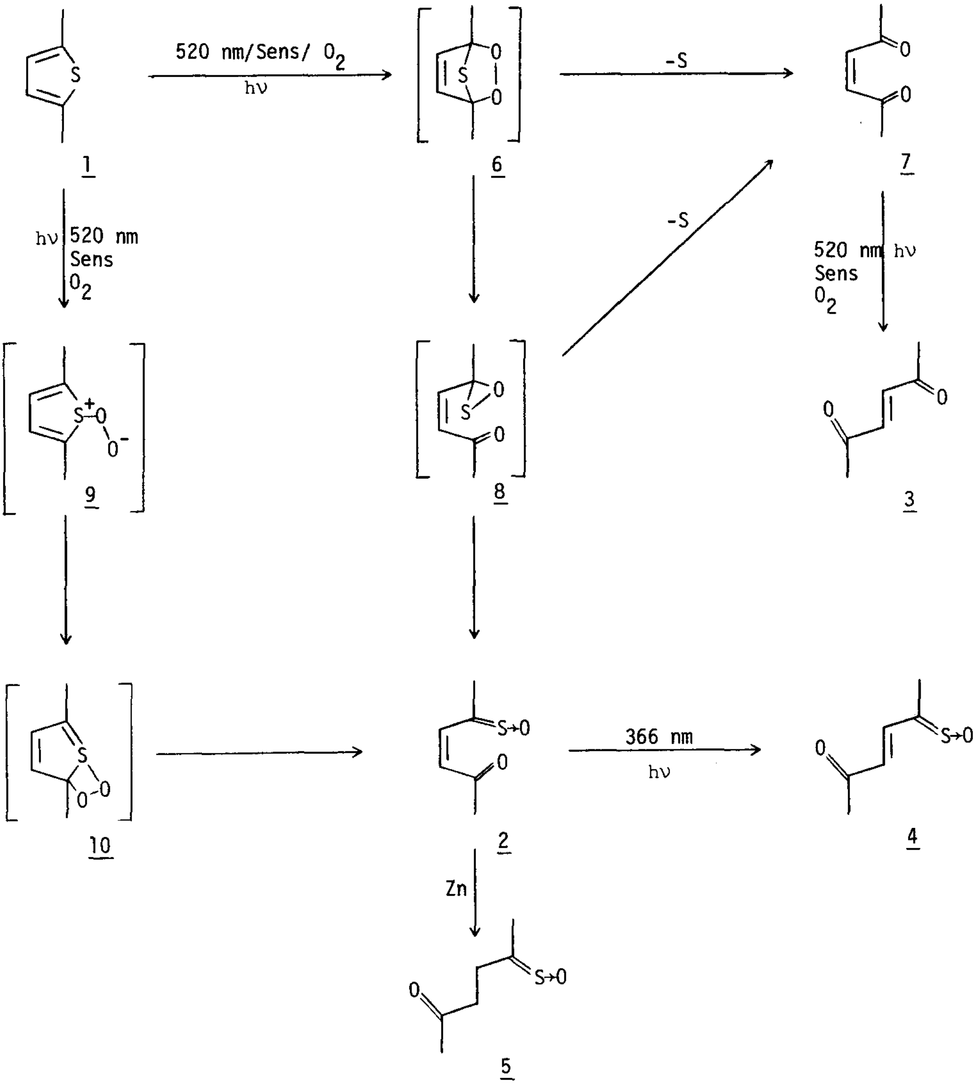
Sulfine 2, mp 30°, showed infrared absorption at 1710 and 1680 cm^{-1} (C=O), 1560 cm^{-1}(C=C), and 1190 and 1130 cm^{-1} ($C=S\rightarrow O$). The ultraviolet spectrum of 2 exhibited a maxium at λ (CH_2Cl_2) 286 nm (ε = 12,300) with a shoulder at 330 nm (ε = 200). Methyl proton resonance for 2 was observed at 2.26 and 2.43 δ while the vinyl protons appeared as an AB quartet centered at 6.40 and

7.53 δ (J_{AB} = 10 cps). In addition, the mass spectrum of 2 (75 ev) showed a parent peak at m/e 144 (21%) and the base peak at m/e 101. On irradiation (366 nm) in degassed chloroform, sulfine 2 was isomerized into its *trans*-isomer 4, mp 20-25°. Sulfine 4 gave resonance in the nmr at 2.28 and 2.41 δ (CH_3 groups) and an AB quartet for the vinyl protons centered at 6.17 and 7.83 δ (J_{AB} = 16 cps). The mass spectrum of 4 showed a parent peak at m/e 144 (18%) and the base peak at m/e 101. Reduction of 2 with zinc dust in methanol containing 85% phosphoric acid gave the dihydrosulfine 5 (oil) in good yield. The nmr spectrum of 5 gave methyl proton resonance at 2.12 and 2.28 δ along with a collapsed A_2B_2 pattern at 2.75 and 2.97 δ for the methylene protons. A parent peak at m/e 146 (9%) was found in the mass spectrum of 5 while the base peak appeared at m/e 71. The identity of the *trans*-diketone 3 was established by comparison of it to authentic material.[5]

Sulfine 2 was found to be photo-inert when irradiated in chloroform solution with 520 nm light absorbed by the sensitizer methylene blue. Furthermore, no significant change in the ratio of sulfine to diketone was observed during the reaction of 1 with singlet oxygen in chloroform. These results, coupled with the marked solvent dependence for diketone formation, suggest that compounds 2 and 3 arise from thiophene 1 by two different pathways.

Lacking additional evidence, it seems reasonable to assume that diketone 3 arises by the Diels-Alder reaction of 1 with singlet oxygen to give an intermediate thioözonide, 6. Rupture of either a C-S or O-O bond in 6 followed by expulsion of sulfur would give the *cis*-diketone 7.[6] Diketone 7[5] has been found to readily isomerize under the reaction conditions into the observed *trans*-product 3. In addition, when the reaction of 1 and singlet oxygen in chloroform solution is carried to 10% completion, a small amount of 7 is detected in the reaction mixture. The thioözonide 6 may also be envisaged as an intermediate in the formation of sulfine 2 since rearrangement of 6 into the oxathiairane 8 followed by ring-opening of the latter would give the sulfine.[6] It should be pointed out that diketone 7 could also arise from the oxathiairane by sulfur extrusion.[7]

An alternative pathway for sulfine formation could occur by attack of singlet oxygen on the sulfur atom of thiophene 1 followed by ring-closure of the resultant sulfoxonium ion 9 to the sulfur ylide dioxetane 10. Ring-opening of the dioxetane would give sulfine 2. Some precedence for this reaction scheme is found in the observations that singlet oxygen reacts with sulfides


1
520 nm/Sens/ O2
hν
6
-S
7
hν 520 nm
Sens
O2
-S
520 nm hν
Sens
O2
9
8
3
10
366 nm
hν
2
4
Zn
5

to give sulfoxides[8] and that dioxetanes undergo ring-opening to give carbonyl species.[9]

Although the exact mechanism by which thiophene 1 reacts with singlet oxygen is not completely understood, it should be noted that products 2 and 3 are formed in extremely clean reactions. Sulfines undergo a variety of interesting transformations such as conversion into sulfoxides when treated with organolithium reagents.[10] Thus, the photoöxidation of thiophene systems might be of considerable synthetic value.

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