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REACTIONS OF SINGLET OXYGEN WITH THIOPHENES

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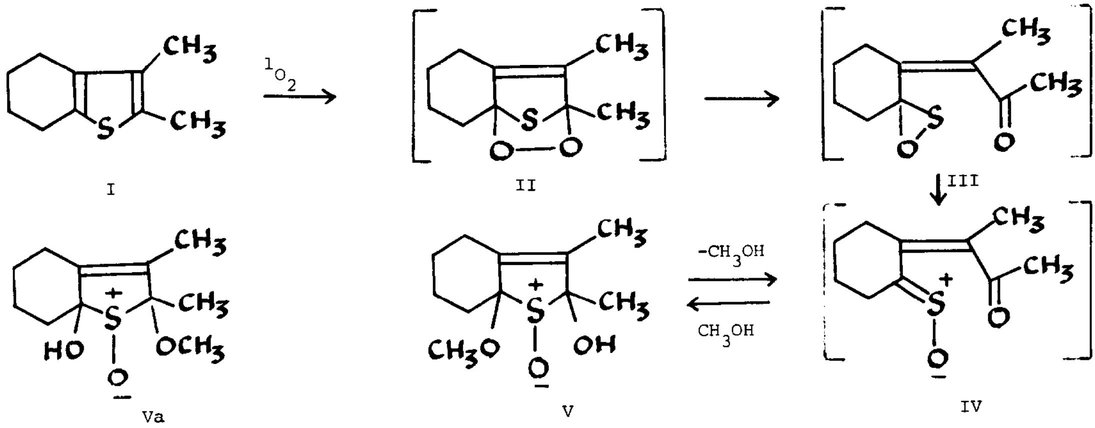
It has been reported[1,2] that thiophene and tetraphenylthiophene, unlike the corresponding furans and pyrroles, are unreactive toward photosensitized autoxidation. We have now found that when thiophenes are substituted with alkyl groups, they do undergo reaction with singlet oxygen, forming sulfines as oxidation products or intermediates.

2,3-Dimethyl-4,5,6,7-tetrahydrothianaphthene[3] (I) (2g) in 1000 ml of methanol was irradiated (275 watt sunlamp) for 10 hr. during oxygenation in the presence of methylene blue. Removal of solvent followed by chromatography on Al_2O_3 (activity II neutral) using petroleum ether as eluent yielded a yellow liquid, b.p.$_{0.01mm}$ 40°C, 200 mg (10%). Calcd. for $C_{11}H_{18}O_3S$: C, 57.38; H, 7.88; S, 14.07. Found: C, 57.64; H, 7.86; S, 13.83. It is assigned structure V based on the spectroscopic data outlined below.

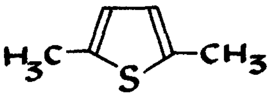
In the ir (CCl_4), V shows peaks at 3565 and 3440, 1450, 1162 and 1075 cm^{-1}. The peak at 1075 cm^{-1}, the most intense absorption in the spectrum, clearly indicates the presence of the $-\overset{+}{S}-\overset{-}{O}$ linkage[4,5]. Nmr peaks are located at τ 6.65 (s, 3H, OCH_3); 7.15 (br s, 1H, D_2O exchangeable); 7.4-8.1 (m, 8H, CH_2); 8.35 (s, 3H, CH_3-C=C-); 8.55 (s, 3H, CH_3-C).

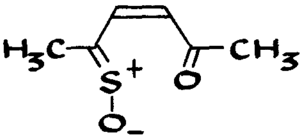


The mass spectrum of V shows a parent peak at m/e 230 and peaks at 199 (loss of OCH_3) and 198 (loss of CH_3OH). The base peak at m/e 155, associated with the loss of both methanol and the CH_3CO fragment, is of particular significance in the assignment of structure, since it distinguishes between structure V and Va. Thus, loss of methanol from Va would produce a sulfine which should not lose the CH_3CO fragment.

While the mechanism of the conversion of I to V remains to be established, it is possible that initial 1,4-addition of oxygen takes place, forming the peroxide II which may decompose through III to yield the intermediate sulfine IV[6,7]. Addition of methanol to IV would yield V.

In the reaction of 2,5-dimethylthiophene with singlet oxygen under similar conditions, methanol was not incorporated, and the sulfine (VI) m.p. 44° could be isolated (ca. 50%). Calcd. for $C_6H_8O_2S$: C, 50.00; H, 5.60; S, 22.10. Found, C, 49.81; H, 5.60; S, 22.48. The uv spectrum in ether contains a maximum at 284 mμ (ε 15,300) with a weaker peak at 224 mμ (ε 4,120). The ir spectrum has bands at 1710, 1675, 1570, 1350,1190 and 1135 cm^{-1}. The peak at 1135 cm^{-1}, one of the strongest in the spectrum, can be correlated with the presence of the C=S=O group[8,9]. The nmr spectrum ($CDCl_3$) has methyl peaks at τ 7.52 (s, 3H); 7.7 (s, 3H); and an AB quartet (2H, J = 10cps) in the vinyl region centered at 2.25 and 3.45. The mass spectrum (70ev) has peaks at m/e 144 (parent), 129, 116, 102, 101 (base peak), and 87.





VI

Formation of the sulfine (VI) has also been observed by Skold and Schlessinger[6] who, using a more intense light source, were able to obtain the product in high yield both in chloroform and methanol.

Further studies on the reactions of singlet oxygen with other sulfur-containing heterocyclic systems are in progress. Support by N.I.H. Grant GM 13854 is gratefully acknowledged.

References

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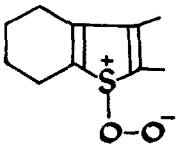
7. Alternatively, the initial attack may involve zwitterionic intermediates of the type



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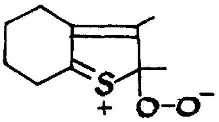

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