

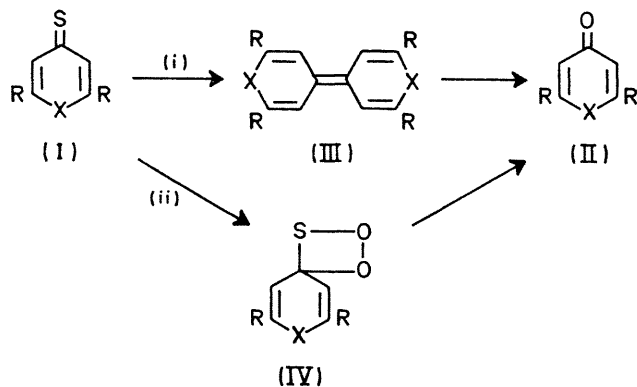
Photosensitized Oxygenation of 4*H*-Pyran-4-thiones and 4*H*-Thiopyran-4-thiones

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Summary Methylene blue-sensitized photo-oxidation of the 4*H*-pyran-4-thiones (Ia—c) and 4*H*-thiopyran-4-thiones (Id, e) gives the corresponding ketones (II).

A TOPIC of current interest in singlet oxygen chemistry¹ is the formation of 1,2-dioxetan.² Most of the work in this field has been concerned with the photo-oxygenation of olefins³ and enamines.⁴ In our previous work⁵ we showed



R	X
(a) H	O
(b) Me	O
(c) Ph	O
(d) H	S
(e) Ph	S

that the photolysis of 2,6-diphenyl-4*H*-pyran-4-thione (Ic) was quenched by a triplet quencher. We now report the

reaction of photogenerated singlet oxygen with 4*H*-pyran-4-thiones and 4*H*-thiopyran-4-thiones.

Irradiation (25 h) of (Ic) in chloroform using methylene blue as sensitizer⁶ gave 2,6-diphenyl-4*H*-pyran-4-one (IIc) in 60% yield. The photo-oxygenation of the other 4*H*-pyran-4-thiones [(Ia) and (Ib)] and the 4*H*-thiopyran-4-thiones [(Id) and (Ie)] under the same conditions resulted in their conversion into the corresponding ketones [(IIa) in 50%, (IIb) in 70%, (IIId) in 50%, and (IIe) in 60% yield]. The identity of the 4*H*-pyran-4-ones and 4*H*-thiopyran-4-ones formed in these photo-oxidations was established by comparison with authentic samples.

Since (Ie) was stable to oxygen in sunlight⁷ and irradiation in the presence of oxygen without the sensitizer gave a polymeric material with only a trace of (IIe), both sensitizer and light are necessary to these photo-oxygenations. The photo-oxidation of (I) to (II) does not take place by path (i). First, irradiation of (I) with light of wavelength 540 nm ($n-\pi^*$) does not yield (III), although $\pi-\pi^*$ excitation of (I) should give (III);⁵ secondly, irradiation of (III) in chloroform, sensitized by methylene blue results in recovery of the starting material.[†] By the analogy to the formation of dioxetan,^{2,3} it is reasonable to assume that (II) arises by the addition of singlet oxygen to the thioketone to give an intermediate (IV). Rupture of the C-S bond in (IV), followed by the formation of SO, results in the formation of (II). SO would be oxidized to SO₂ and this was detected by flushing the reaction mixture with oxygen and passing the products through a vanadate-silica gel column.⁸ The structure of (IV) is supported by the fact that the photo-oxidation of 2,6-diphenyl-4-diphenylmethylene-4*H*-thiopyran⁹ resulted in formation of both benzophenone and (IIe). It should be noted that the low ionization potential

† After irradiation of a very dilute solution of (IIIc), only a trace of (IIc) was detected by u.v. and t.l.c. (silica gel).

of thioketones[‡] would cause them to react with singlet oxygen as readily as olefins.^{3a}

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[‡] Although the ionization potential of pyrone derivatives has not been determined, substitution of the oxygen of a ketone with sulphur results in a substantial decrease of the ionization potential.¹⁰

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