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

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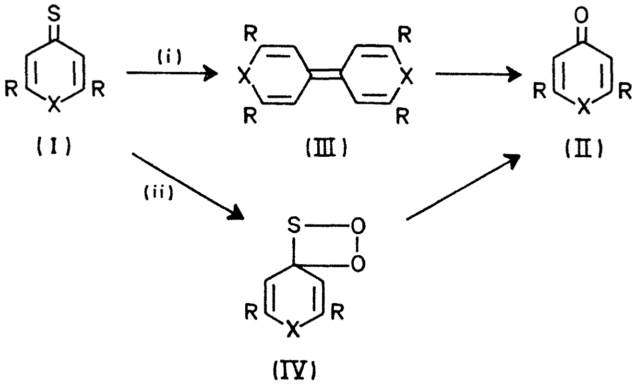
Summary Methylene blue-sensitized photo-oxidation of the 4*H*-pyran-4-thiones (Ia—c) and 4*H*-thiopyran-4-thiones (Id, e) gives the corresponding ketones (II).

A TOPIC of current interest in singlet oxygen chemistry[1] is the formation of 1,2-dioxetan.[2] Most of the work in this field has been concerned with the photo-oxygenation of olefins[3] and enamines.[4] In our previous work[5] we showed 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.



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

Irradiation (25 h) of (Ic) in chloroform using methylene blue as sensitizer[6] 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%, (IId) 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 sunlight[7] 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–π^*) does not yield (III), although π–π^* 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 SO_2 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*-thiopyran[9] resulted in formation of both benzophenone and (IIe). It should be noted that the low ionization potential

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† 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]

We thank Professor K. Teramura for his interest in this study.

(*Received, October 27th*, 1970; *Com.* 1870.)

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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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