Photolysis of Dihydrothiophen-3(2*H*)-ones

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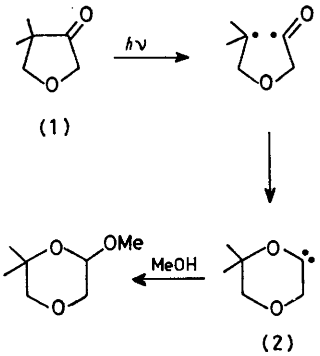
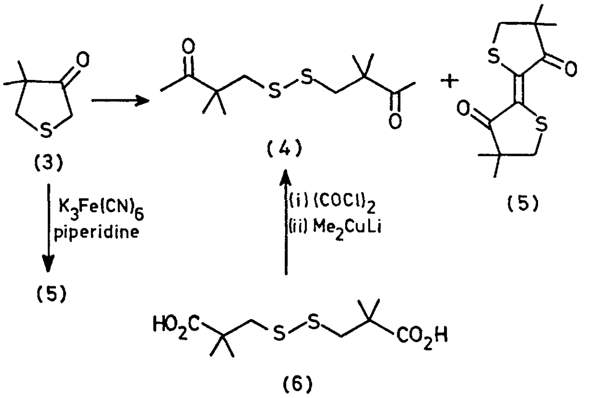
Summary Photolysis of dihydrothiophen-3(2*H*)-ones in methanol proceeds *via* β-cleavage to give 5,6-dithia-2,9-decanediones.

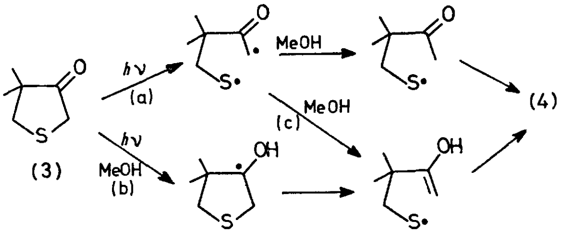
In previous studies of the photochemistry of carbocyclic ketones the structural factors that influence the formation of oxacarbene-derived products have been elucidated.[1] The work of Collins *et al.*[2] has revealed that additional factors are involved in oxacarbene formation from 3-oxacycloalkanones and we have recently reported[3] on an investigation of the photochemistry of dihydrofuran-3(2*H*)-ones that showed that oxacarbene formation occurs as a major process only when the substitution pattern leads to cleavage of the C(3)–C(4) bond [*e.g.*, (**1**) → (**2**)].



We now report on an investigation of the photochemistry of dihydrothiophen-3(2*H*)-ones, the sulphur analogues of the dihydrofuran-3(2*H*)- ones. Irradiation of 4,4-dimethyldihydrothiophen-3(2*H*)-one (**3**)[4] in methanol gave (**4**) (81%) and (**5**) (2%).† The structure of (**4**) was established by its independent synthesis from (**6**);[5] that of (**5**) was established by comparison with a sample prepared by oxidation of (**3**).[6]



Thus the photolysis of (**3**) follows a different course from that of its oxygen analogue (**1**). The major product (**4**) is formed by cleavage of the S–C(2) bond (*β*-cleavage) rather than by *α*-cleavage.‡ Preference for this process must be dictated by the relatively high stability of the thiyl radical, and the pathways in the Scheme can be envisaged.

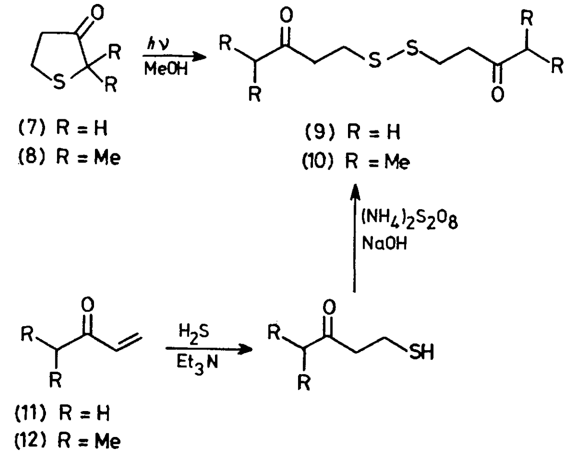


Scheme

Irradiation of (**3**) in CH_3OD gave $[^2H_2]$-(**4**) with deuterium incorporated as DCH_2CO–, which can be interpreted in terms of either pathway (b) or (a)—(c). Irradiation of (**3**) in t-butyl alcohol led only to the recovery of starting material, suggesting that the formation of (**4**) in methanol can best be interpreted in terms of pathway (b).

The yield of the minor product (**5**) was not influenced by degassing of the solution, suggesting that it does not arise *via* autoxidation of (**3**), but *via* hydrogen abstraction from C(2) by a radical formed from (**3**) followed by coupling and further hydrogen abstraction from C(2).

The photochemistry of the dihydrothiophen-3(2*H*)-ones (**7**)[4] and (**8**)[7] was also investigated. In methanol these formed (**9**)[8] and (**10**), respectively, the analogues of (**4**), albeit in lower yield.§ The structures of these products were established by their independent synthesis from (**11**) and (**12**), respectively.[9] In the case of (**7**) irradiation in t-butyl alcohol also led to the formation of (**9**), although the yield was only 7% compared to 23% in methanol. This suggests that here primary *β*-cleavage of type (a) can occur with the resulting diradical giving (**9**) by abstraction of hydrogen from (**7**) or some derived species.



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† Irradiations were carried out in Pyrex for 1% solutions in the presence of sodium carbonate with an Hanovia 450 W medium pressure lamp. All new compounds were characterized by elemental or mass spectrometric analysis and by i.r. and ^1H n.m.r. spectroscopy.

‡ *Cf.* J. R. Collier and J. Hill, *Chem. Comm.*, 1968, 700; 1969, 640; W. C. Lumma, Jr., and G. A. Berchtold, *J. Org. Chem.*, 1969, **34**, 1566, for related exocyclic cases and K. Schaffner and O. Jeger, *Tetrahedron*, 1974, **30**, 1891 for a general discussion of photochemical *β*-cleavage of ketones.

§ Irradiation of (**7**) in Freon-113 has previously been reported to give a complex mixture containing thiophen and dihydrothiophen derivatives (K. K. Maheshwari and G. A. Berchtold, *Chem. Comm.*, 1969, 13).

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