Photolysis of 4-Substituted Isoxazolin-5-ones: Sulphur-stabilized Iminocarbenes

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Summary Photolyses of 4-sulphenylated 2,3-dimethylisoxazolin-5-ones proceed *via* iminocarbene intermediates which are trapped with methanol to give pyruvic aldehyde thioacetals

THE intermediacy of iminocarbenes has been implicated in numerous photolytic and thermal reactions[1–3] Recent work[3,4] has demonstrated that some of these species are completely interconvertible with antiaromatic 1*H*-azirine intermediates prior to their undergoing other potential reactions such as Wolff rearrangement or hydrogen shifts Although direct evidence of iminocarbene species has recently been obtained by e s r spectroscopy at low temperatures,[5] chemical trapping of these species has not been reported because of their rapid intramolecular reactions

We now report on the photochemistry of isoxazolin-5-ones, which are reasonable precursors of iminocarbenes The 4-substituted isoxazolin-5-ones (**2a**—**h**)† were conveniently

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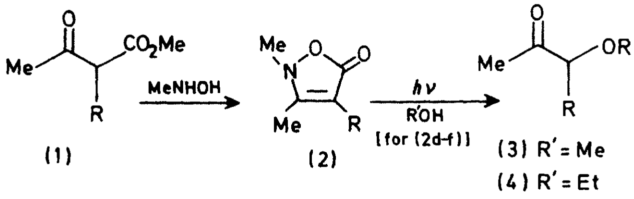
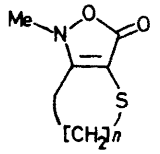
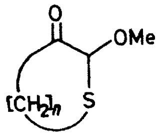
† All new compounds gave satisfactory analytical and spectral data

prepared by treating the corresponding *β*-keto esters (**1a**—**h**)[6] with *N*-methylhydroxylamine.[7] Irradiation‡ of (**2a**) in methanol led only to its complete recovery, and similar irradiation of (**2b**) and (**2c**) resulted in slow decomposition with no products being detectable. In sharp contrast, irradiation of the 4-phenylthioisoxazolinone (**2d**) in methanol under the same conditions resulted in rapid disappearance of starting material and gave (**3d**) in 49% yield: i.r. 1720 cm^{-1}; n.m.r. δ ($CDCl_3$) 2·08 (s, 3H), 3·59 (s, 3H), 4·96 (s, 1H), and 7·3 (m, 5H). Irradiation of (**2d**) in ethanol similarly gave (**4d**) (40%). This reaction was observed generally for the other 4-sulphenylated isoxazolinones (**2e**—**h**) (Table). Irradiation of the bicyclic compounds (**5a**), m.p. 80—81 °C, and (**5b**), m.p. 88—90 °C, in methanol afforded the cyclic ketothioacetals (**6a**) (56%) and (**6b**) (58%), respectively, and unidentified minor products.





(5) a, *n* = 2
b, *n* = 3



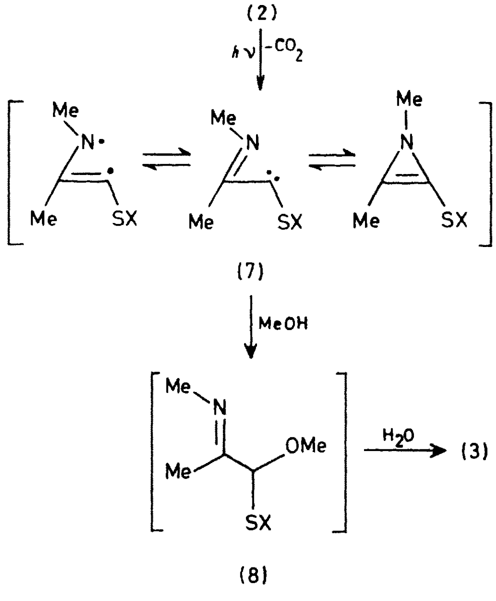
(6) a; *n* = 2
b, *n* = 3

Table. Photolyses of the isoxazolinones (**2**) in methanol.

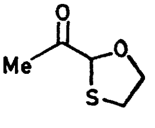
Isoxazolinone (**2**)	M.p./°C	Product[a]	Yield/%[b]
a; R = H	37—38		
b; R = Cl	85—86		
c; R = OPh	101—102		
d; R = SPh	73—74	(**3d**)	49
e; R = S-*β*-naphthyl	145—146	(**3e**)	23
f; R = $SCH_2CH{=}CH_2$	Oil	(**3f**)	28
g; R = SCH_2CH_2OH	67—68	(**3g**)[c]	71
h; R = SCH_2CH_2OAc	Oil	(**3h**)	47

[a] All products were isolated as oils and were identified by ^{1}H n.m.r. and i.r. spectroscopy, and elemental analyses. [b] Yields are based on isolated products. [c] This exists predominantly in the cyclic hemiacetal form.

The formation of *α*-ketothioacetals can be explained by the sequence shown in the Scheme. The iminocarbenes (**7**) generated by photochemical extrusion of carbon dioxide are substantially stabilized by the adjacent sulphur substituent,[8] and may have a long enough lifetime to be trapped by the solvent (methanol) before they could undergo intramolecular reactions. The resulting imines (**8**) may then be hydrolysed to give the products, although prior hydrolysis of the iminocarbenes to ketocarbenes cannot be ruled out at this stage. In accordance with the above mechanism, photolysis of (**2g**) in an inert solvent (benzene) gave the oily thioacetal (**9**) (18%) by intramolecular trapping.



Scheme.



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(*Received, 30th June* 1980; *Com.* 705.)

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‡ All photolyses were carried out at ambient temperature under argon with a Pyrex-filtered 100 W high-pressure mercury lamp.

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