Photocyclisation of *NN*-Dialkyl α-Thioxoamides. Selective γ-Hydrogen Abstraction by the Thiocarbonyl Group

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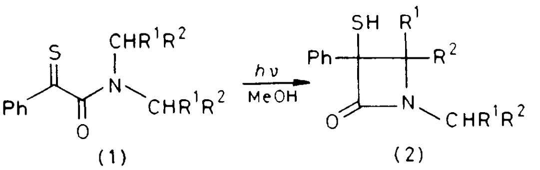
Summary *NN*-Di-isopropyl and *NN*-s-butyl-α-phenylthioxoacetamides (**1a**) and (**1b**) undergo γ-hydrogen abstraction rather than δ-hydrogen abstraction on irradiation to give the corresponding β-lactams (**2a**) and (**2b**) respectively, while irradiation of *NN*-diethyl-α-phenylthioxoacetamide (**1c**) yields the disulphide (**3c**); the selective γ-hydrogen abstraction may be explained in terms of an electron transfer mechanism.

Photocyclisation of thiones has been studied extensively by de Mayo *et al.*[1] They have reported that acyclic thiones undergo δ-hydrogen transfer† specifically on irradiation to give cyclopentane-thiols, and that thiones lacking δ-hydrogen atoms are inactive toward photolysis.[1b] Thiones undergo γ-hydrogen abstraction only when they possess no δ-hydrogens and the γ-hydrogens are activated by heteroatoms.[1c]

Recently, we reported the photocyclisation of α-oxoamides[2] and αβ-unsaturated amides.[3] We now report the photocyclisation of α-thioxoamides which are isoelectronic with these amides. In this reaction, selective γ-hydrogen abstraction took place in spite of the presence of δ-hydrogen atoms.



(1)
a; $R^1 = R^2 = Me$
b; $R^1 = Me, R^2 = Et$
c; $R^1 = H, R^2 = Me$

(2)
a; $R^1 = R^2 = Me$
b; $R^1 = Me, R^2 = Et$

When *NN*-di-isopropyl-α-phenylthioxoacetamide (**1a**) was irradiated in methanol with a high pressure mercury lamp (> 300 nm), the 3-mercapto-azetidinone (**2a**) was produced *via* γ-hydrogen abstraction in 38% yield. The structure of (**2a**) was determined by elemental analysis and spectral data, in particular the close similarity of the n.m.r. spectrum of (**2a**) to that of the corresponding 3-hydroxy-compound.[2] Photolysis of the *NN*-di-s-butylthioxoamide (**1b**) also gave the corresponding lactam (**2b**)‡ (25%). In both cases, no δ-hydrogen abstraction products were isolated. These results indicate that these thioxoamides undergo γ-hydrogen abstraction selectively in contrast to thiones. The lactam (**2a**) was not detected when (**1a**) was irradiated in the *nπ** region of the thiocarbonyl group (*ca.* 585 nm), although many unidentified products were produced. This suggests that the photocyclisation of the thioxoamides proceeds from the upper excited states as in the case of thiones.[1]

Although γ-hydrogen abstraction is quite common in the photochemistry of carbonyl compounds,[4] it is extremely rare in that of thiones.[5] Consequently, the selective formation of the β-lactams *via* γ-hydrogen abstraction is of

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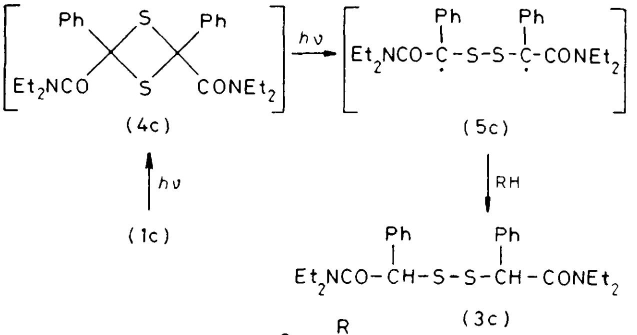
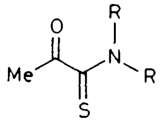
† de Mayo *et al.* suggested that the photoreaction of thiones might proceed *via* a concerted $2_\sigma + 2_\pi$ process rather than δ-hydrogen abstraction.

‡ Although spectral data confirm the structure of (**2b**) the elemental analysis was relatively poor because the product was a mixture of stereoisomers and did not crystallize.

interest both mechanistically and synthetically.[6] The difference in reactivity of the thioamides and the thiones may be explained by an electron transfer mechanism.[7] Electron transfer from the amide nitrogen to the excited thiocarbonyl group may occur prior to hydrogen shift. This is supported by the fact that thiocarbonyl groups are better electron acceptors than carbonyl groups,[8] and that electron transfer from the amide nitrogen to the excited carbonyl group has been presumed to play an important role in the photocyclisation of β-oxoamides.[9]

However, photolysis of the *NN*-diethylthioxoamide (**1c**) afforded the disulphide (**3c**) in 48% yield instead of the corresponding β-lactam. The structure of (**3c**) was confirmed by an independent synthesis from *NN*-diethyl-1-chlorophenylacetamide and Na_2S_2. The formation of (**3c**) can be explained in terms of the dimerisation of (**1c**) and subsequent reductive decomposition of the resulting dithietan (**4c**). Photochemical[10] and thermal[11] dimerisation of α-thioxoamides to dithietans and photochemical conversion of dithietans into disulphides[12] have been reported. The direct formation of the biradical (**5c**) from (**1c**) is also conceivable. The fact that photolysis of (**1a**) or (**1b**) yields the lactam rather than the disulphide is explained by the steric hindrance due to the substituents on nitrogen. The bulky substituents are presumed to inhibit dimerisation and thus make inefficient γ-hydrogen abstraction possible. This is consistent with the fact that photoreaction of (**1c**) is much more efficient than that of (**1a**) or (**1b**). Finally, the α-oxothioamides (**6a**) and (**6b**) were completely inert towards photolysis.





(6)

a; R = Et

b; R = CH_2Ph

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[11] K. Thim, W. Schmueser, and J. Voss, *J. Chem. Res.*, 1977, (*M*) 2837, (*S*), 244; W. Schmueser and J. Voss, *ibid.*, 1978, (*M*), 1901, (*S*), 149. The synthesis of α-thioxoamides is described in these papers.

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