Photochemical Reaction of *N,N*-Dialkyl-α,β-unsaturated Thioamides

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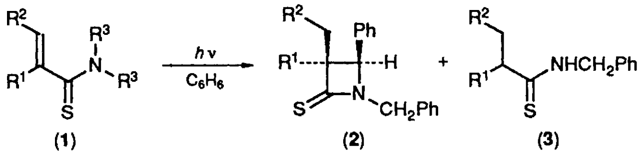
Irradiation of *N,N*-dibenzyl-α,β-unsaturated thioamides leads to cyclisation involving γ-hydrogen abstraction by the alkene unit *via* a zwitterionic intermediate.

The photochemistry of nitrogen-containing thiocarbonyl compounds such as thioamides and thioimides has received much attention because these compounds show considerably different photochemical behaviour from that of amides and imides;[1] it may also lead to useful syntheses of some heterocycles. We have already reported that the photochemical reactions of acyclic and semicyclic thioimides proceed *via* hydrogen abstraction and [2 + 2] cycloadditions.[2] We now report the photochemical reaction of *N,N*-dialkyl-α,β-unsaturated thioamides which involves Type II cyclisation *via* zwitterionic intermediates.

The thioamides (**1a–f**) were obtained by the reaction of the corresponding amides with Lawesson's reagent almost quantitatively. The *N,N*-dialkylmethacrylthioamides (**1a–c**) were inert towards photolysis. However, when the *N,N*-dibenzylmethacrylthioamide (**1d**) was irradiated with a high-pressure mercury lamp under nitrogen, the azetidinethione (**2d**) and the debenzylated thioamide (**3d**) were obtained in 59 and 26% yields, respectively. Photolysis of the thioamides (**1e**) and (**1f**) gave the azetidinethiones (**2e**) and (**2f**) as the main products. The stereochemistry of the azetidinethione (**2e**) was determined on the basis of its ^{1}H NMR spectra to be solely *cis*.†

The mechanism for the formation of (**2**) and (**3**) may involve the zwitterionic intermediate (**4**).[2c,3] Irradiation of the thioamide (**1e**) in the presence of isobutylamine (0.1 M) gave the thioamide (**3e**) in a yield (29%) nearly equal to that of (**2e**) (30%). If the azetidinethione were formed *via* the thioketene and imine[4] generated by a Type II cleavage process, isobutylamine would trap the thioketene to yield *N*-isobutylmethacrylthioamide.[5] However, this compound was not detected. These results indicate that the azetidinethione (**2**) and the thioamide (**3**) are formed from the same species, which is not a



				Yield (%)	
	R^1	R^2	R^3	(**2**)	(**3**)
a	Me	H	Me	Recovered	
b	Me	H	Et	Recovered	
c	Me	H	Pr^i	Recovered	
d	Me	H	CH$_2$Ph	59	26
e	Me	Me	CH$_2$Ph	56	Trace
f	–[CH$_2$]$_4$–		CH$_2$Ph	41	31

Scheme 1

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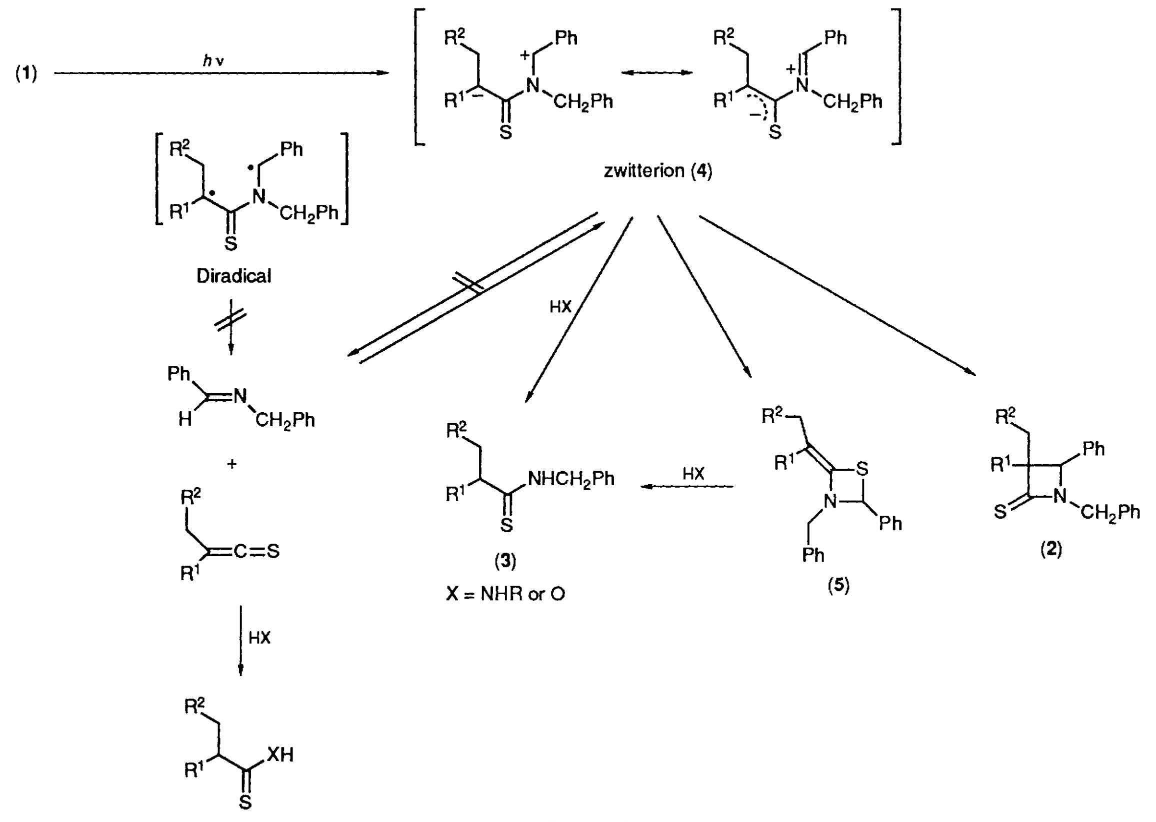
† The configuration of the azetidine-2-thione (**2e**) was determined on the basis of its ^{1}H NMR spectrum which exhibited signals at δ 0.48 (t, *J* 7.4 Hz, 3H, 3-Et), 1.1–1.2 (m, 1H, 3-Et), 1.25 (s, 3H, 3Me), 1.4–1.5 (m, 1H, 3-Et), 3.96 and 5.35 (AB, *J* 14.4 H$_z$, 2H, N–CH$_2$), 4.50 (s, 1H, 4-CH), and 7.0–7.3 (m, 10H, aromatic).



Scheme 2

diradical intermediate but rather the zwitterion (**4**). It is suggested that the thioamide (**3**) is formed by intermolecular trapping of the zwitterion (**4**) with nucleophiles, with intramolecular attack of the anion giving the azetidinethione (**2**) as shown in Scheme 2. It has been reported that zwitterionic intermediates generated from thioketenes and imines yielded 1,3-thiazetidines in some cases.[4] For the formation of the thioamides (**3**), it is not yet possible to rule out absolutely a mechanism involving hydrolysis of the 1,3-thiazetidines (**5**) as a minor path.

The cyclisations were not sensitised by 3-methoxyacetophenone (E_T 72 kcal mol^{-1}; 1 cal = 4.184 J)[6] and Michler's ketone (E_T 62 kcal mol^{-1}).[6] Quenching of the reactions by 2,5-dimethylhexa-2,4-diene (E_T 58.7 kcal mol^{-1}),[6] *trans*-stilbene (E_T 50 kcal mol^{-1}),[6] or ferrocene (E_T 35 kcal mol^{-1})[7] was inefficient. These results indicate that the photoreactions proceed from the π–π^* singlet excited states.

It is known that the photolysis of α,β-unsaturated amides gives azetidine-2-ones *via* addition of ketenes to imines produced by a Type II cleavage reaction.[5] In view of this it is interesting that change of the carbonyl group to the thio analogue leads to different photochemical behaviour. Furthermore, although the photochemistry of thioenones[1c] and other α,β-unsaturated thiocarbonyl compounds such as α,β-unsaturated dithioesters[8] and thiouracil derivatives[9] has been studied, this previous work involved intermolecular cycloaddition with alkenes, hydrogen abstraction, and dimerisation involving the sulphur atom of the thiocarbonyl chromophore to give a diradical intermediate, and there is no previous example to the best of our knowledge of an alkene unit conjugated with a thiocarbonyl group taking place in photochemical reactions.

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