

Photochemical Isomerisation of β,γ -Unsaturated Thioimides to 2-Thiabicyclo[2.1.0]pentanes

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Photolysis of *N*-acetyl-2,2-dimethylbut-3-enethioanilides **1** gave

1-(*N*-acetylanilino)-5,5-dimethyl-2-thiabicyclo[2.1.0]pentanes **2** in good yields *via* intramolecular [2 + 2] cycloaddition of the thiocarbonyl group across the alkene; the corresponding amides were inert towards photolysis.

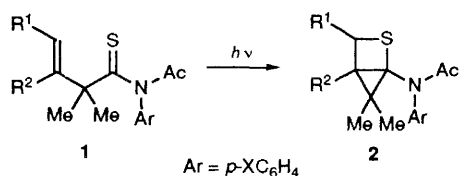
The interest of β,γ -unsaturated carbonyl compounds to photochemists can be attributed to the proximal incorporation of the alkene and carbonyl chromophores in these molecules. These materials undergo virtually all the photochemical reactions known for isolated ketones or alkenes, and several unique reactions as well.¹ Aside from intramolecular oxetane formation, the presence of both chromophores in a single molecule leads to two unique reactions: the 1,3-shift and the 1,2-shift or oxa-di- π -methane rearrangement.

Photochemical studies of thiocarbonyl compounds have received much attention from both the mechanistic and the synthetic points of view since their photochemical behaviour differs from that of the corresponding carbonyl derivatives.² For compounds containing both alkene and thiocarbonyl chromophores, we have already reported that irradiation of γ,δ - and δ,ϵ -unsaturated thiocarbonyl molecules led to intramolecular [2 + 2] cyclisation and C-S bond formation followed by 1,4-hydrogen shift.³ The photochemistry of β,γ -unsaturated thiones is limited to studies on thioenamides in which the alkene and thiocarbonyl chromophores were connected *via* nitrogen.⁴ We now report the photochemical reaction of β,γ -unsaturated thioimides which involves [2 + 2] cycloaddition and leads to a rare type of compound, the 2-thiabicyclo[2.1.0]pentanes.

The thioimides **1a-f** were obtained by the reaction of the corresponding amides with Lawesson's reagent⁵ followed by acetylation with acetyl chloride and triethylamine. Irradiation of compound **1a** with a high-pressure mercury lamp under argon gave the thiabicyclopentane **2a** in 85% yield as the sole product. Photolysis of the other thioimides **1b-f** gave the corresponding bicyclic thietanes **2b-f** as shown in Table 1. The structures of **2a-f** were determined from spectral data and elemental analyses. The presence of pairs of resonances in their ¹H and ¹³C NMR spectra showed that they each existed as a mixture of two rotamers at room temperature; their NMR spectra in (CD₃)₂SO above 100 °C showed style peaks. For

Table 1 Photolysis of unsaturated thioimides **1**

	R ¹	R ²	X	Yield of 2 (%)
a	H	H	H	85
b	H	H	Me	93
c	H	H	MeO	82
d	H	H	Cl	91
e	-[CH ₂] ₃ -		Cl	82
f	-[CH ₂] ₄ -		Cl	95



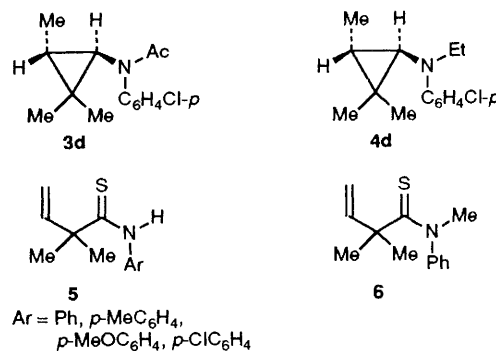
example, the ¹H NMR spectrum of **2d** showed three doublets at δ 3.27, 2.37 and 1.94 assignable to 3-CH₂ and 4-CH; alkene proton resonances were absent. The ¹³C NMR spectrum shared triplet, doublet and two singlet peaks due to C-3, C-4, C-1 and C-5 at δ 20.7, 33.8, 27.6 and 52.8, respectively, and there was no signal for the thiocarbonyl carbon atom.† The structures were further supported by chemical reactions: **2d** was desulfurised by Raney Ni to give **3d** in 77% yield, reduction of which with LiAlH₄ led to the cyclopropylamine **4d** (76%), structures **3d** and **4d** being determined from their spectral data.

The cyclisation was sensitised by Michler's ketone and by thioxanthone; quenching by stilbene or ferrocene was inefficient.⁶ This reaction is presumed to involve a triplet state by direct irradiation.

Finally, irradiation of *N*-mono- and *N,N*-di-substituted β,γ-unsaturated thioamides **5** and **6** showed that they were inert under the same conditions, contrasting with the results for the β,γ-unsaturated thioimides **1**, the yields of cyclopropane-fused thietanes **2** from which were largely independent of substituents of both alkene and aryl groups. The present reaction provides the first example of β,γ-unsaturated thiocarbonyl compounds in which the alkene and thiocarbonyl groups were connected *via* carbon, and is a useful synthesis of the 2-thiabicyclo[2.1.0]pentane skeleton, which, to the best of our knowledge, has not hitherto been synthesised.⁷

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† ¹H and ¹³C NMR spectra were measured at 150 and 100 °C, respectively, in (CD₃)₂SO.



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