Photochemical Synthesis: Quinolines

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Summary In a new photochemical reaction of the thiocarbonyl function, *N*-(*o*-styryl)thioamides are converted into quinolines.

ALTHOUGH the photochemistry of thiones is now well established,[1] that of the thioamides is barely touched upon.[2] We report here an intramolecular cycloaddition of substituted thioanilides which gives quinolines as the immediately isolable product. The synthesis has a particular advantage in that it is achieved by the linking of three simple groups which bear the substitution required for the final product.

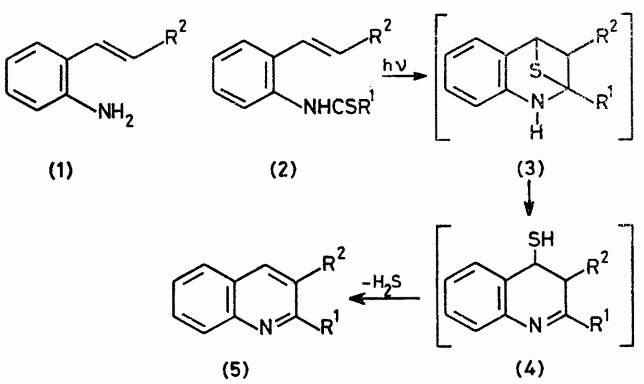
The styryl amine precursors (**1**) (here with an unsubstituted aromatic ring) were prepared by the versatile Heck synthesis[3] or by rearrangement of *N*-allylaniline.[4] The formation of the amide and thence the thioamide[5] (**2**) controlled the nature of the substituent R^1 at the 2-position in the final quinoline. Irradiation† of (**2**) in acetonitrile at ambient temperatures then gave the quinolines (**5**) (Table).

TABLE. Yields of quinolines.

Reactant	Irradiation time/h	Yield/%[a]
(**2a**)	3·5	69
(**2b**)	8	44
(**2c**)	2·5	46
(**2d**)	27	58

[a] Based on material consumed.

The quantum yield of formation of the quinoline derived from (**2a**) is $1{\cdot}3 \pm 0{\cdot}02 \times 10^{-2}$, with excitation at 278 ± 8 nm and this was unaffected when (**2a**) was irradiated in the presence of the low energy triplet quenchers ferrocene (E_T 43 kcal/mol[6]) and 3,3,4,4-tetramethyldiazetine *NN'*-dioxide (E_T <42·4 kcal/mol[7]).‡ The reaction could not be sensitised by triphenylene (E_T 66·5 kcal/mol). We therefore conclude that the reaction proceeds *via* a singlet state. If, as is most probable, this is the lowest singlet, then by available analogy§ this is $\pi \rightarrow \pi^*$. A possible mechanism for the reaction is *via* the thietan (**3**) and the thiol (**4**). The absorption spectrum shows at long wavelength a smooth conversion, with an isosbestic point, from starting material into product. The changes at short wavelength could be compatible with the Scheme; we are attempting to identify the intermediates concerned.



SCHEME
a; $R^1 = R^2 = Me$
b; $R^1 = Me$, $R^2 = Ph$
c; $R^1 = Me$, $R^2 = CN$
d; $R^1 = Ph$, $R^2 = Me$

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† The preparative irradiations were carried out with a 450 W Hg arc with a Pyrex filter after degassing by freeze–pump–thaw cycles.

‡ 1 cal = 4·184 J.

§ The lowest singlet transition in thioacetamide is π,π^* (see J. Barrett and F. S. Deghaidy, *Spectrochim. Acta*, 1975, **31A**, 707) and substitution of the nitrogen is unlikely to lower the n,π^* state below that of the thioamide π,π^* state or that of the styrene; see, however, M. J. Janssen, *Rec. Trav. chim.*, 1960, **79**, 454.

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