

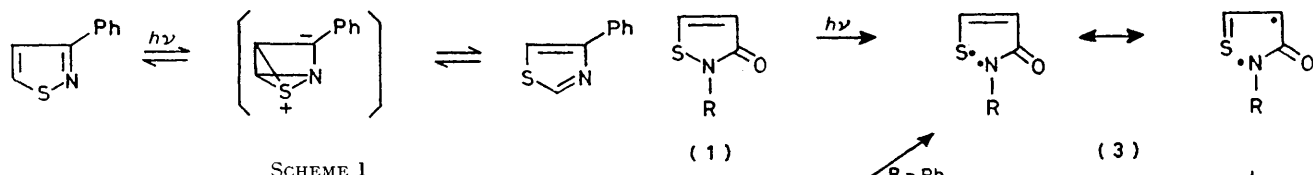
**Photoisomerization of 2-Substituted-isothiazol-3(2*H*)-ones to
3-Substituted-thiazol-2(3*H*)-ones**

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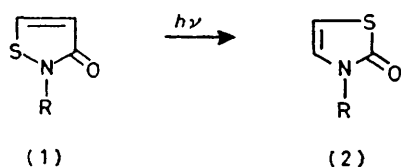
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Summary The photoisomerization of isothiazol-3(2*H*)-ones yields thiazol-2(3*H*)-ones, possibly by a ring contraction-ring expansion mechanism involving an initial homolytic step.

THE photoisomerization of isothiazole to thiazole has been reported to occur in low yield.¹ Phenyl- and diphenyl-isothiazoles gave thiazoles on irradiation,² and the reverse conversion has been described.³ A common intermediate has been suggested for these rearrangements (Scheme 1).



We report here the photochemical behaviour of some non-aromatic isothiazoles. Irradiation of 2-substituted-isothiazol-3(2*H*)-ones (**1**) in benzene for 24 h with a 450 W Hanovia lamp (Pyrex-filtered) afforded good yields of 3-substituted-thiazol-2(3*H*)-ones (**2**) (Scheme 2). The generality of the reaction is illustrated by the variety of the substituents R. Except for (**2a**), the photoproducts (**2**) have not been previously reported. The easy availability of the starting materials of type (**1**),⁴ coupled with the high yield of the photoisomerization, makes it a synthetically attractive route to this class of compounds.

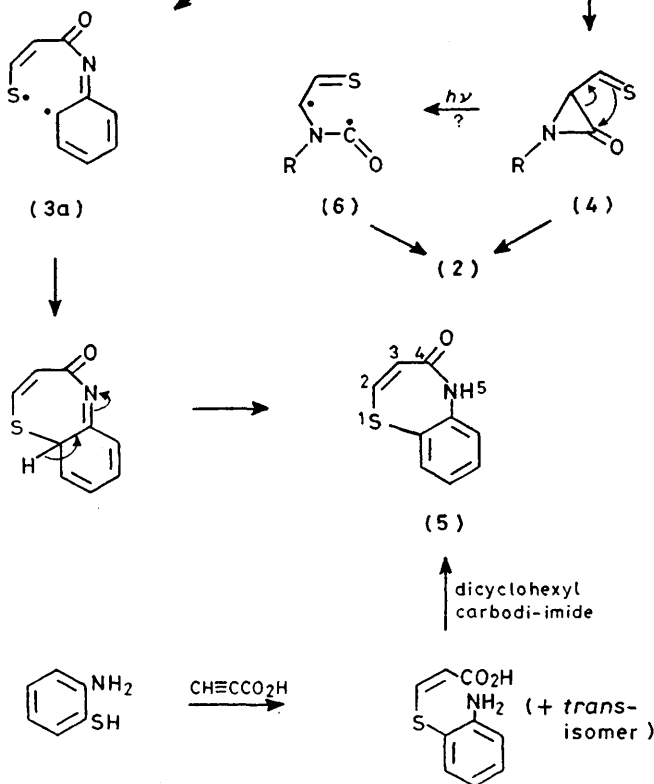


R	Compound ^a	M.p./°C	% Yield ^c
Ph	(2a)	65–67 ^b	88
PhCH ₂	(2b)	40–42	80
ClCH ₂ CH ₂	(2c)	Oil	71
Bu [†]	(2d)	36–37	73
Cyclohexyl	(2e)	47–49	70

^a Readily identified by n.m.r., i.r., u.v., and mass spectroscopy; elemental analyses confirm the assignment. ^b Lit. m.p. 70–71 °C (G. Ottmann, H. Hoberecht, and H. Hooks, Jr., *Angew. Chem. Internat. Edn.*, 1967, **6**, 1073). N.m.r. and mass spectrum are identical to those reported. ^c Yields of pure isolated compounds.

The most reasonable mechanism for the reaction (Scheme 3) involves a ring contraction, followed by a ring expansion. The photoexcited molecule yields, through a homolytic cleavage of the weakest bond in the molecule (S–N), the diradical (**3**) which cyclizes to an α -lactam (**4**) which, in turn, ring expands to the product (**2**), either thermally or by a subsequent photochemical step.[†]

α -Lactams have been proposed as intermediates in the isomerization of 3-hydroxyisoxazoles to oxazol-2(3*H*)-ones⁵ and 5-imino-2,3,4-triphenylisoxazoline to 1,4,5-triphenyl-imidazolone.⁶ In the photolysis of (**1a**) we have found supporting evidence for the homolytic step proposed by isolating a small amount of compound (**5**), which is probably formed as shown in Scheme 3 from the diradical (**3a**).



Anilino radicals are well known to react at the *ortho* position, as in the photolysis of *N*-acylanilines to yield *o*- and *p*-acylaniline,⁷ or the photolysis of 1-phenylbenzotriazole to yield carbazole.⁸

The structure of (**5**) (m.p. 188–189 °C) was suggested by its spectral data: n.m.r., δ (CD₃SOCD₃) 6.25 (d, *J*_{2,3} 10 Hz, 3-H), 7.13 (d, *J*_{3,2} 10 Hz, 2-H), 7.3 (4H, m, ArH) and 10.25 (br s, exchanges with D₂O, NH); i.r., ν_{\max} (KBr) 1670 (C=O) and 2900–3200 (complex; NH); *m/e* 177 (*M*⁺). The structure was proved unambiguously by comparison with an authentic specimen (m.p. 188–189 °C) prepared independently from *o*-aminobenzenethiol and propiolic acid (Scheme 3).

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[†] A diradical intermediate, which subsequently loses CO, has been suggested in the photochemical conversion of α -lactams into imines (J. C. Sheehan and M. N. Nafissi-V., *J. Amer. Chem. Soc.*, 1969, **91**, 1176). In the present case, such a diradical intermediate (**6**) has an alternative course of reaction open, namely reclosure to form (**2**).

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⁴ S. N. Lewis, G. A. Miller, M. Hausman, and E. C. Szaborski, *J. Heterocyclic Chem.*, 1971, **8**, 571.

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⁸ E. M. Burgess, R. Carithers, and L. McCullagh, *J. Amer. Chem. Soc.*, 1967, **90**, 1923.