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

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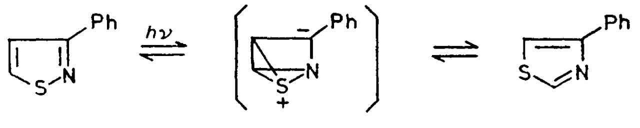
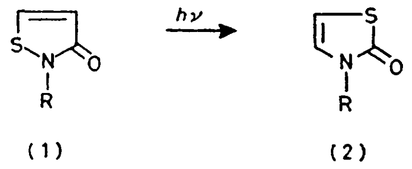
Summary The photoisomerization of isothiazol-3(2*H*)-ones yields thiazol-2(3*H*)-ones, possibly by a ring contraction–ring expansion mechanism involving an initial homolytic step.

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



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.



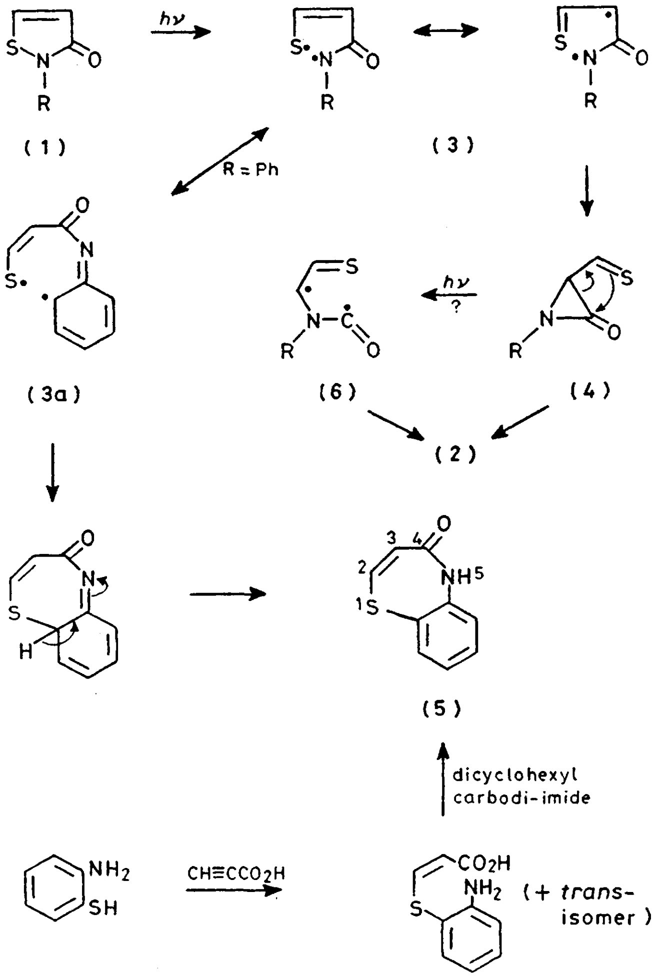
Scheme 2

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^t	(**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*)-ones[5] and 5-imino-2,3,4-triphenylisoxazoline to 1,4,5-triphenylimidazolone.[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]



Scheme 3

The structure of (**5**) (m.p. 188—189 °C) was suggested by its spectral data: n.m.r., δ (CD$_3$SOCD$_3$) 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 D$_2$O, N*H*); 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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