Photoisomerization of Phenylisothiazoles

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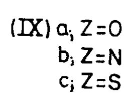
Summary The photoisomerization of phenylisothiazoles into phenylthiazoles probably proceeds *via* tricyclic sulphonium cation intermediates.

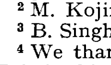
CATTEAU and his co-workers have reported the photorearrangement of isothiazole into thiazole,[1] and Kojima and Maeda have studied thiazole–isothiazole photorearrangements.[2] We have investigated the photoisomerization of 3- and 5-phenylisothiazole (I and II) and of 3,5-diphenylisothiazole (III) in order to establish differences between the behaviour of isothiazoles and of isoxazoles[3] upon irradiation.

(I) R = H
(III) R = Ph

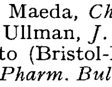
(VIII) a; R = H
b; R = Ph



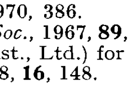
(IV) R = H
(V) R = P



(II)



(VIII)



(IX) a; Z = O
b; Z = NMe
c; Z = S

Vycor-filtered low-pressure mercury-arc irradiation of (I)[4] in dry ether for 45 min. gave, along with recovered (I) (72%), 4-phenylthiazole (IV)[5] in 12% yield. Irradiation of (II)[6] under similar conditions produced (I) in 2·3% yield, together with recovered (II) (35%). In an irradiation under similar conditions of (III), 2,4-diphenylthiazole (V)[6] was produced in 48% yield and 25% of the starting material was recovered.

Although the exact mechanism is not yet clear, it is obvious that the ring-contraction–ring-expansion mechanism, as in the case of 3,5-diarylisoxazole–2,5-diaryloxazole rearrangements,[3] or Wynberg's intermediates[7] in the 2-phenylthiophen–3-phenylthiophen isomerization cannot rationalize the above results. Considering the results for thiazole–isothiazole photorearrangements,[2] tricyclic sulphonium cation intermediates (VIIa) and (VIIb) are the most probable intermediates,† as shown in the Scheme. The photorearrangement products so far studied seem to be produced from the most stable intermediate (VII) in which the negative charge is stabilized by resonance with the phenyl group. It is noteworthy that in a series of compounds (IX; Z = O,[2] N,[8] and S), only (IXa) undergoes the ring-contraction–ring-expansion sequence upon irradiation, whereas the others (IXb, IXc) undergoes valence-bond tautomerism. Detailed studies on this mechanism are now proceeding, based on molecular orbital calculations.

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† Analogous intermediates were suggested by Kojima (ref. 2) for the photoisomerizations of thiazoles.

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