A NEW APPROACH TO THE MECHANISM ON PHOTOREARRANGEMENTS OF THIAZOLES

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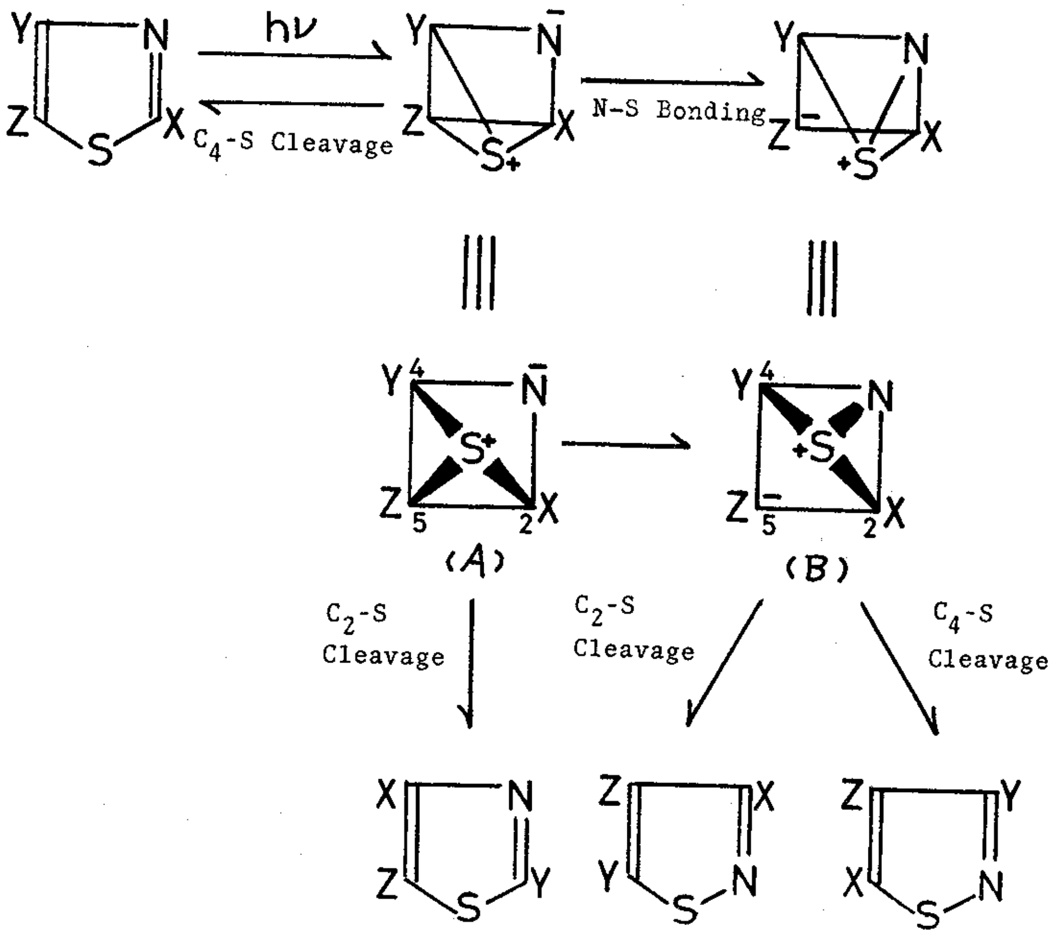
A possible mechanistic rationalization of the photorearrangements of phenylthiazoles was suggested in the previous paper to involve the formation of a set of bicyclic isomers (valence bond isomers) or tricyclic sulphonium cation intermediates.

Based on considerable information accumulated about the photochemical behaviour of various substituted thiazoles, the mechanistic aspect of the reactions are discussed and we present a mechanism via tricyclic sulphonium cation intermediates (A and B). Support for our newly proposed mechanism is provided by deuterium incorporation observed on irradiation of 2-phenylthiazole or 4-phenylthiazole to 3-phenylisothiazole.

Further, this mechanism provided a satisfactory qualitative explanation for all the observed results.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C_4-S Cleavage
N-S Bonding
(A)
(B)
C_2-S Cleavage
C_2-S Cleavage
C_4-S Cleavage
Y
N
Z
X
S
4
5
2