Tetrahedron Letters No.52, pp. 5315-5317, 1967. Pergamon Press Ltd. Printed in Great Britain.

THE PHOTOISOMERIZATION OF 1,4,5-TRIMETHYLIMIDAZOLE AND 1,3,5-TRIMETHYLPYRAZOLE

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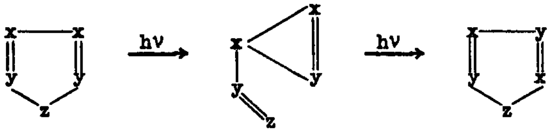
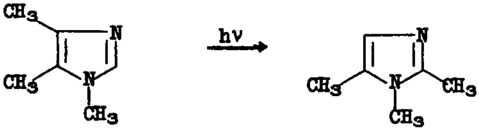
(Received in USA 23 August 1967)

A ring-contraction ring-expansion sequence was established by Ullman and Singh (1) for the photoisomerization of 3,5-diphenylisoxazole to 2,5-diphenyloxazole. Although the uncertainties involved in drawing analogies for photochemical reactions suggest caution (2), it is interesting that similar processes provide convenient rationales for many of the photolytic interchanges of two contiguous atoms in five-membered heteroaromatic compounds. Examples include the photoconversions of indazoles to benzimidazoles (3), pyrazole to imidazole (3), 2-arylthiophenes to 3-arylthiophenes (4), and pyrazolinones to hydantoins (5), as well as the conversion of other isoxazoles to oxazoles (6). We wish to report the photoisomerizations of 1,4,5-trimethylimidazole (I) to 1,2,5-trimethylimidazole (II) and of 1,3,5-trimethylpyrazole (III) to 1,2,4-trimethylimidazole (IV). The formation of II from I requires a different process than that described by Ullman and Singh (1).



Irradiation of an ethanolic solution of I for 42 hrs. with a low-pressure mercury-vapor lamp gave a 36% yield of a 5:1 mixture II:I. The product ratio was determined from the nmr



I

II

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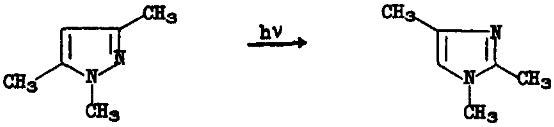
spectrum (7) and II was identified by isolation as the picrate (8) and by the nmr spectrum of the methiodide.

Photolysis of an ethanolic solution of III for 3 hrs. with a high-pressure mercury-vapor lamp gave an 11% yield of IV. The isolated imidazole IV was identified by its nmr spectrum (7)

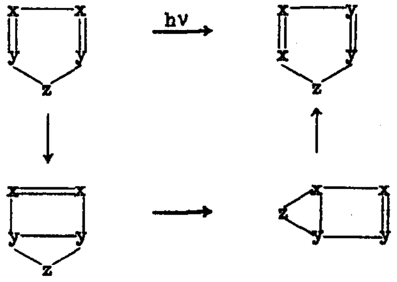


III IV

and by direct comparison with authentic material as the picrate (9).

These reactions may be added to the relatively few examples studied (3a) (4) of photoconversion of a five-membered heteroaromatic which is unsubstituted by another chromophore. The influence of such a chromophore on the photochemistry of these systems is illustrated by the fact that 1-methyl-4,5-diphenylimidazole does not react upon photolysis with a low-pressure mercury lamp in ethanol solution (10).

The photoisomerization of I to II cannot be rationalized by interchange of atoms at positions 2 and 3 (x and y) of the heteroaromatic ring. Although such a process, occurring twice, can account for the photoisomerization of III to IV, more straightforward pathways can be envisioned. For example, a pathway involving V and VI accounts for both results and seems reasonable (11, 12)



V VI

although other possibilities, analogous to those suggested to account for the photoisomerizations of benzenes (13) and some arylthiophenes (4), cannot be ruled out with the available data. The mechanism and scope of these reactions are under further investigation.

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