Tetrazole Photochemistry: The Question of Ring-transposition

By Peter Scheiner*

(*York College, City University of New York, Jamaica, New York* 11432)

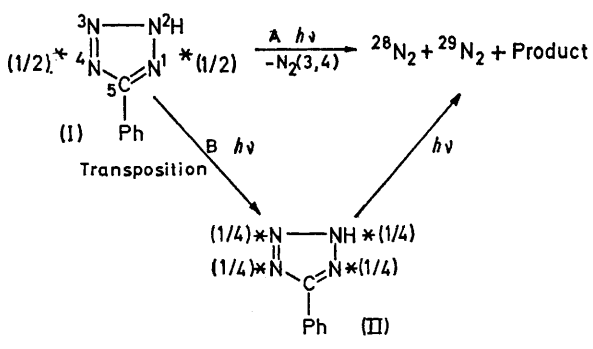
and W. M. Litchman

(*University of New Mexico, Albuquerque, N. Mexico* 87106)

Summary Using ^{15}N n.m.r. spectroscopy it has been demonstrated that, unlike other aromatic heterocycles, photochemical ring-transposition does not occur in the 5-phenyltetrazole system.

Numerous examples of photochemical ring-transposition of 5-membered aromatic heterocycles have been described.[1] Recently, van Tamelen and Whitesides proposed a general reaction scheme to rationalize the diversity of reported results.[1] The tetrazole system, a fully aromatic heterocycle, might also be expected to undergo this type of isomerism. However, direct observation of tetrazole ring-transposition is rendered difficult by four ring nitrogens and consequent structural degeneracy. The mechanism has now been investigated by means of ^{15}N n.m.r. spectroscopy.

Photolysis of 5-substituted tetrazoles ultimately results in the loss of one equivalent of nitrogen and formation of dihydro-*s*-tetrazine products[2,3] (The corresponding tetrazolide anions photolyse in an entirely different manner.[2,4]). Using ^{15}N-labelled 5-phenyltetrazole (I) (one ^{15}N per molecule distributed equally at positions 1 and 4) the photolytically evolved gas was found to consist of 50% $^{28}N_2$ and 5·% $^{29}N_2$.[3] The evolved nitrogen may therefore be viewed as originating from positions 3 and 4 of the ring (path A). Or *via* transposition, the ^{15}N label could become completely scrambled (II) prior to nitrogen expulsion (path B). In the latter case, precisely the same mass analysis for the liberated nitrogen would be observed. These paths may be distinguished by determining whether or not ring-transposition occurs during photolysis.



The ^{15}N n.m.r. spectrum[†] of (I) (2·7M, Me_2SO revealed a single, unsplit[‡] peak at 84·85 p.p.m. upfield from reference $^{15}NO_3^-$. It should be noted that positions 1 and 4 of the 5-substituted tetrazole nucleus are indistinguishable due to ready proton tautomerism; similarly positions 2 and 3 cannot be differentiated. An authentic sample of (II) possessing ^{15}N label at all ring positions was prepared by the method of Finnegan[5] *et al.*, using labelled potassium azide ($^{15}NNN^-$). Compound (II) showed two resonance peaks at 26·04 and 84·85 p.p.m. upfield from $^{15}NO_3^-$. Thus the chemical shifts for N^1, N^4 (84·85 p.p.m.) and N^2, N^3 (26·04 p.p.m.) were established.

To determine the extent of ring-transposition (path B), (I) (0·06M, EtOH, 254 mμ) was irradiated to 40% reaction, as measured by nitrogen evolution. Undecomposed tetrazole was recovered, recrystallized, and its ^{15}N n.m.r. spectrum recorded. The recovered irradiated material had only one peak at 84·85 p.p.m.; no indication of a signal was observed at 26·04 p.p.m. It is therefore apparent that ring-transposition with attendant scrambling did not occur to a detectable extent.

This result and those reported previously[3] are only compatible with photodecomposition by path A, expulsion of nitrogen from positions 3 and 4. Although the initial photolytic ring-opening may well lie along a potential transposition path, nitrogen loss intervenes before significant interchange of ring positions in the starting material. In this respect tetrazole differs from related polyhetero 5-membered aromatic systems, such as oxazole[6] and imidazole.[7]

The author (P.S.) gratefully acknowledges the support of the City University Research Foundation.

(*Received*, 30*th March*, 1972; *Com.* 542.

[†] Varian XL-100, 10·1 MHz, using Fourier transform.

[‡] Failure to observe ^{15}N–H splitting results from rapid proton exchange.

[1] E. E. van Tanelen and T. H. Whitesides, *J. Amer. Chem. Soc.*, 1971, **93**, 6129.
[2] P. Scheiner, *J. Org. Chem.*, 1969, **34**, 199.
[3] P. Scheiner and J. F. Dinda, *Tetrahedron*, 1970, **26**, 2619.
[4] P. Scheiner, *Tetrahedron Letters*, 1969, 4863; 1971, 4489.
[5] W. G. Finnegan, R. A. Henry, and R. Luftquist, *J. Amer. Chem. Soc.*, 1958, **86**, 3908.
[6] M. Kojima and M. Maeda, *Tetrahedron Letters*, 1969, 2379.
[7] P. Beak, J. L. Miesel, and W. R. Messer, *Tetrahedron Letters*, 1967, 5315.