

PHOTOLYSIS OF VIC-TRIAZOLES

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An interest in derivatives of 4-phenyl-1,2,3-triazole, 1, as a source for either phenylethynyl nitrene, 2, or phenylcyanocarbene, 3, brought about an investigation of the photolysis of 1 and 4-phenyl-5-bromo-1,2,3-triazole, 4, (1). A marked increase in photosensitivity was achieved by the introduction of the C-bromo substituent.

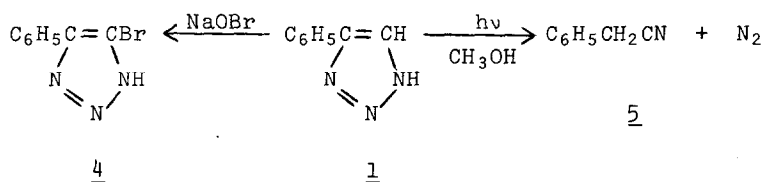
A deoxygenated solution of 1 (1.45g, 10.0 mmole) in 400 ml of methanol was irradiated under nitrogen for 130 hours in a Rayonet unit with low-pressure mercury lamps at 2537 Å (2). Removal of methanol left a brown viscous liquid (1.75g) from which 0.41g (35% yield) of phenylacetonitrile, 5, was isolated by chromatographic separation on a column of silica gel and eluted with benzene-hexane mixtures. Further elution with chloroform gave 0.36g of an intractable resin.

By vpc the crude product mixture was separated into four volatile components in the ratio of 1:1:1.5:50 using a carbowax column. The major component with a retention time of 12.0 min. proved to be identical with 5. Each of the other three had a lower retention time and accounted for less than one percent of product. They have not been identified.

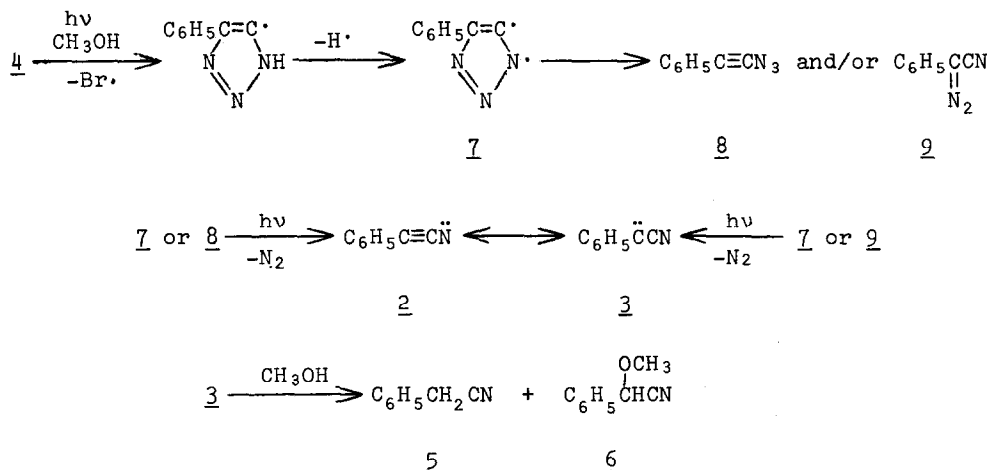
In a similar way a solution of 4 (1.12g, 5.0 mmole) in 500 ml of methanol was irradiated under nitrogen for 22 hours in a Rayonet unit with low-pressure mercury lamps at 2537 Å (2). Following removal of the solvent a dark tar (0.45g) remained insoluble in chloroform. The chloroform extracts were washed with sodium bisulfite solution and with water and dried over calcium chloride before removing the solvent. The liquid residue (0.26g) was fractionated by vpc with a preparative column, SE-30.

Of six volatile components obtained from the mixture, the first and the fifth were present in trace amounts and have not been identified. In the order of appearance from the column, the second compound was acetophenone (2%) followed by methyl benzoate (10.2%), phenylacetonitrile, 5, (19.5%) and α -methoxyphenylacetonitrile, 6, (6.5%) (3). All products were identified by vpc, ir, nmr and mass spectral data, each of which gave perfect comparison with authentic data.

The present work appears to provide the first example of a photolytic cleavage of the vic-triazole ring when unsubstituted at nitrogen (4). Neither simultaneous nor sequential cleavage of two ring bonds has been established; however, in either event phenylacetonitrile, 5, is apparently produced from 1 by a rearrangement. To establish mechanistic detail further work is planned.



Since 4-phenyl-1,2,3-triazole, 1, undergoes photolysis slowly, it is assumed that the more rapid photo-reaction of 4 is initiated by homolytic cleavage of the carbon to bromine bond. This was confirmed by the formation of 1 as its hydrobromide salt upon irradiation of 4 in anhydrous ether. Either simultaneous or subsequent hydrogen abstraction from nitrogen leaves a residue which may be a triazole aryne, 7, or its isomers, either phenylethynyl azide, 8, (5) or α -diazo- α -phenylacetonitrile, 9. With elimination of nitrogen from 8 or 9, the formation of 2 and 3 respectively would be expected (6). The nitrene, 2, and the carbene, 3, are contributors to a resonance hybrid which apparently reacts as the carbene by hydrogen abstraction to form 5 and by insertion to form 6 (7). Additional work is planned to account for the formation of methyl benzoate, (6) and acetophenone.



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References

1. Previously unknown, colorless 4-phenyl-5-bromo-1,2,3-triazole, 4, m.p. 158.5-159.5°C was prepared from 4-phenyl-1,2,3-triazole, 1, by treatment with sodium hypobromite according to a general procedure described by R. Hüttel and G. Welzel, Ann. 593, 207 (1955). As expected 4 is acidic and forms salts with alkali. Strong ir absorption at 3450 cm^{-1} is characteristic of the NH bond. A sharp singlet in the nmr spectrum of 1 in (acetone- d_6) at $\delta 8.25$ (1 proton), assigned to the triazole CH is not found in the nmr spectrum of 4 in (acetone- d_6). Two sets of multiplets for phenyl protons are found at $\delta 7.98$ (2H) and $\delta 7.45$ (3H) for 1 and at $\delta 7.98$ (2H) and $\delta 7.50$ (3H) for 4. Calculated for $\text{C}_8\text{H}_6\text{N}_3\text{Br}$: C, 42.85; H, 2.67; N, 18.75; Br, 35.71. Found: C, 43.02; H, 2.66; N, 18.81; Br, 35.71.
2. Before irradiation the solution was degassed by bubbling through it a stream of nitrogen for 6 hours.
3. The percentages represent yield of reaction.
4. M. E. Hermes and F. D. Marsh, J. Am. Chem. Soc., 89, 4760 (1967) report ring-chain tautomerism between 1-cyano-1,2,3-triazole and α -diazo-N-cyanoethylideneimine. O. Dimroth, Ann., 335, 1 (1904) discusses tautomerism between certain hydroxytriazoles and α -diazoamides. J. H. Boyer and L. T. Welford, J. Am. Chem.

Soc., 80, 2741(1958) describe a solvolytic opening of the triazole ring in pyridotriazole. E. M. Burgess, R. Carithers and L. McCullagh, J. Am. Chem. Soc., 90, 1923(1968) describe the formation of ketenimines and indoles from certain monocyclic N-substituted vic-triazoles by photolysis.

5. Phenylethynyl azide has been considered to be an intermediate for the formation of trans-dicyanostilbene from an iodine azide adduct of phenylethynyl bromide and iodine azide on treatment with zinc (J. H. Boyer and S. Selvarajan, 154th National Meeting of the American Chemical Society, Chicago, 1967; Chemical and Engineering News 45, No. 41, 52(1967)).
6. Spin multiplicity for $2 \leftrightarrow 3$ is undetermined.
7. Phenylcyanocarbene, generated by photolysis of certain phenylcyanooxiranes was "trapped" by reacting with methanol to form 6 (P. C. Petrellis, H. Dietrich, E. Meyer and G. W. Griffin, J. Am. Chem. Soc., 89, 1967(1967)). By private communication, Professor Griffin reports that 5 and methyl benzoate are also produced.