

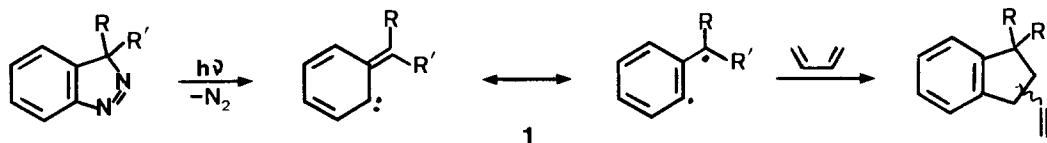
1,3-DIRADICAL INTERMEDIATES IN 3H-PYRAZOLE PHOTOLYSES: 1,4 ADDITION TO DIENES¹

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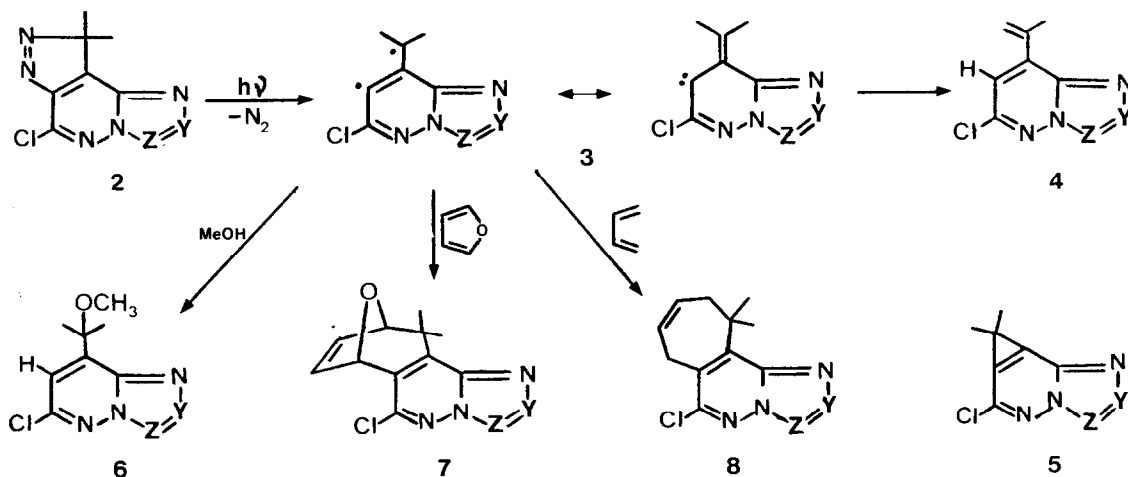
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Summary: The photolyses of pyrazolopyridazines (2a-c) lead to alkenes (4a-c). With added methanol, furan or buta-1,3-diene, intermediates (3a-c) are trapped as compounds (6a-c) - (8a-c) respectively.

The photolyses of 3H-pyrazoles provide a useful and well studied synthesis of cyclopropenes.² By comparison the photodeazetation of analogues in which the olefinic bond is part of an aromatic system has received less attention.³ Closs and co-workers have shown that such



photolyses give intermediates, e.g. (1), which are often triplet entities.⁴ Unlike their acyclic counterparts,² the carbene form of (1) is not favoured because of the loss of resonance stabilisation; trapping experiments with buta-1,3-diene provide only products of 1,3-diradical addition and then only to an ene component of the diene.⁴ We now report on the photochemically induced loss of nitrogen from the heteroaromatic pyrazolopyridazines (2a-c). The resultant



a) Y = Z = CH; b) Y = N; Z = CH; c) Y = CH; Z = N

diradicals (3a-c) are trapped by furan and buta-1,3-diene to give the novel heterocycles (7a-c) and (8a-c) respectively. To our knowledge, these provide the first examples of 1,4-addition by such intermediates.

Direct irradiation (350 nm) of the known⁵ ten electron aromatic heterocycles (2a-c) results in the ejection of nitrogen from the 3H-pyrazole moiety. The conjugated alkenes (4a-c) are formed⁶ as expected from this type of substrate,^{3,4,7} but in low yields. Unlike their 3H-indazole analogues^{3,4,7} compounds (2a-c) do not give isolable isomeric ring-closed cycloproparenes (5a-c) either from reaction at ambient or low temperatures. Cyclopropaheteroarenes thus remain unknown. When the photolyses are performed in methanol, diradicals (3a-c) are diverted to the side-chain ethers (6a-c) in good (36-64%) yields^{5,6} and these compounds are easily separated (column chromatography) from alkenes (4a-c) which are present to an extent of 30-10%.

Photodeazetation of (2a-c) in furan leads to trapping of diradicals (3a-c) as the novel tetracycles (7a-c) which are formed as the major products of reaction in excellent (56-70%) yields;⁶ alkenes (4a-c) are present to an extent of ca. 10%. That these additions occur in a 1,4- and not a 1,2-fashion is evident from the spectroscopic data of the products. In particular, the sp³-hybridised bridgehead H-C-O moieties of (7a-c) display in their nmr spectra proton doublets ($J \approx 1.7$ Hz) at ca. 4.7 and 5.5 ppm, and carbon doublets at ca. 77.1 and 88.2 ppm for the allylic and bis-allylic centres respectively; any 1,2-addition to furan by either the diradical or carbene forms of (3a-c) would generate only one such H-C-O entity. The diradical intermediates (3a-c) can also be trapped by buta-1,3-diene. Once again, 1,4-addition of intermediates (3a-c) to the diene is observed as evidenced by the formation⁶ of the cycloheptadiene derivatives (8a-c) (40-55%). Minor products (<15%) analogous to those derived from (1) and buta-1,3-diene were also isolated in the present study.

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References and Footnotes:

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