Photolysis of Tetrazolo[1,5-*b*]pyridazines; Formation of Cyanocyclopropenes

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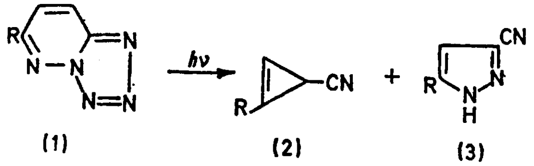
Summary Irradiation of tetrazolopyridazines affords 3-cyanocyclopropenes (20—25%) and 3-cyanopyrazoles (0·1%) by elimination of two or one molecules of nitrogen, respectively.

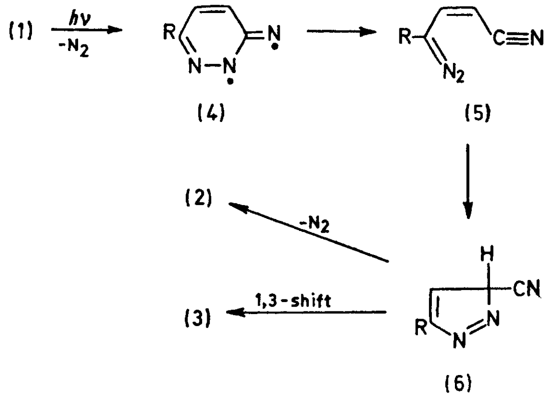
There have been many reports on the photolysis of pyridazines[1] and their *N*-oxides,[2] and some interesting results have been reported concerning polyaza-compounds such as tetrazoles[3] and triazoles.[4] However, photolysis of tetrazolopyridazines has not hitherto been described. We now report that irradiation of tetrazolopyridazines affords cyanocyclopropenes and cyanopyrazoles.



a; R = Me, b; R = H

Tetrazolopyridazines[5] (1) were irradiated (200w, high-pressure Hg lamp) in dichloromethane for 6—7 h, and the reaction mixtures were worked-up in the usual way. From (1a) were obtained 3-cyano-1-methylcyclopropene (2a), an oil (20—25%), b.p. 60°/10 mmHg (bath temp.), and 3-cyano-5-methylpyrazole (3a), m.p. 112—113° (0·1%). From (1b) was obtained 3-cyanocyclopropene (2b), an oil (*ca.* 25%), b.p. 55°/10 mmHg (bath temp.). The formation of (3b) was detected by g.l.c. and t.l.c., but its isolation was difficult on account of the very low yield. The i.r., n.m.r., and mass spectra support the structures assigned in all other cases.

In every case, *ca.* 20% of the starting material was recovered, but prolonged irradiation caused extensive decomposition and decreased the yields of the cyanocyclopropenes and cyanopyrazoles. When MeOH was used as solvent, similar results were obtained. On the other hand, when acetone was used as solvent, the yield of cyclopropenes was low (*ca.* 5%) and pyrazoles were not obtained. The starting materials were consumed in 3—4 h irradiation.



The formation of cyclopropenyl ketones[2b] and acylpyrazoles[2a] on the photolysis of pyridazines and their *N*-oxides has already been reported, and it is interesting that in the present work, cyano-derivatives of the same ring systems were obtained.

It is known that in solution tetrazolopyridazines exist completely in the tetrazole form, rather than in the tautomeric azide form.[6] By analogy with the case of other azo-compounds, N_2 might be eliminated† from (1), followed by the formation of cyano-diazo-compound (5) *via* diradical (4). Ring closure of (5) gives (6), followed by elimination of N_2 to give (2) which by a 1,3-shift of a hydrogen atom forms (3).

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† Evolution of N_2 was observed during irradiation.

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