Tetrahedron Letters No. 34, pp.3211 - 3212, 1971. Pergamon Press. Printed in Great Britain

PHOTOLYSIS OF 6-AZIDO-AZOLOPYRIDAZINES

B. Stanovnik

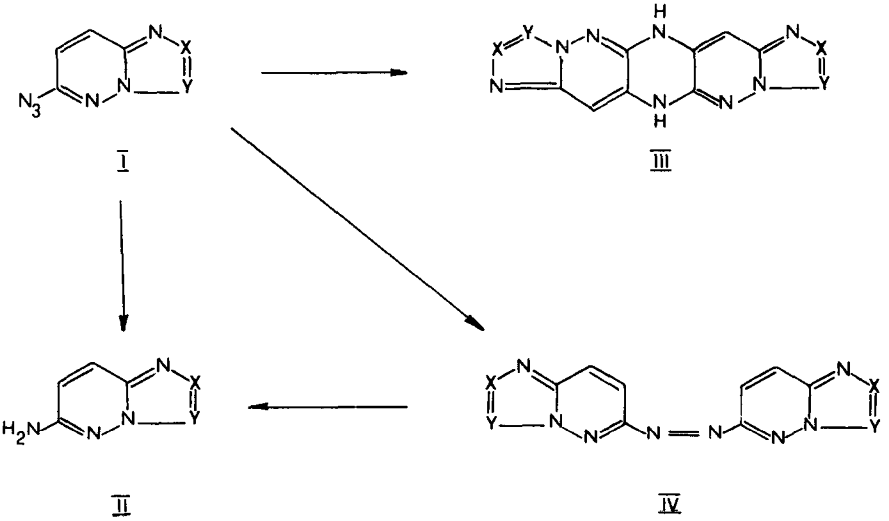
Department of Chemistry, University of Ljubljana, Ljubljana, Yugoslavia

(Received in UK 15 July 1971; accepted for publication 20 July 1971)

A paper[1] which has appeared recently describing tetrazolo-azido transformations of 6-azido-tetrazolo/1,5-b/pyridazine and photochemical and thermal reactions of similar types of compounds, prompted us to publish our observations on photochemical reactions of 6-azido-azolo-pyridazines at this stage.

Photolysis of organic azides results in the formation of electron-deficient species nitrene, which stabilizes by a variety of routes. Hydrogen abstraction from carbon α to the nitrogen, hydrogen abstraction from the solvent resulting in amine formation, double bond insertion and coupling with the formation of azocompounds[2] are the most general reactions.

Photolysis of 6-azido-azolo-pyridazines (I) afforded three types of products: 6-amino-azolo-pyridazine (II), pentacyclic compound (III) and azocompound (IV).



When 6-azido-s-triazolo/4,3-*b*/pyridazine[3] (I; X=N, Y=CH) (100 mg in 20 ml of EtOH) in cylindrical quartz tube was irradiated in Rayonet photochemical reactor using 16 8W RUL-3500 A° lamps for 20 hours, a mixture, separated by thick layer chromatography, of 86 % of 6-amino-s-triazolo/4,3-*b*/pyridazine (II; X=N, Y=CH), identical in m.p. and ir with an authentic sample prepared according to lit.[4], 10 % of 6H,13H-di-s-triazolo/4,3-*b*:4',3'-*b'*/pyrazino/2,3-*e*:5,6-*e'*/dipyridazine (III, X=N, Y=CH),/m.p. > 350°, ir (KBr) NH 3220 cm^{-1}, nmr in conc. D_2SO_4 τ = 0,85 (H_3,H_{10},s) τ = 1,87 (H_7,H_{14},s), high resolution m.s. m/e = 266,07751, calcd.for $C_{10}H_6N_{10}$ (m/e = 266,077686), 1-2 % of azocompound (IV; X=N, Y=CH), (m.p.>350°) which was reduced quantitatively to II (X=N, Y=CH) with $Na_2S_2O_4$ and <1 % of polymeric material (m.s. m/e >600).

6-Azidoimidazo/1,2-b/pyridazine[5] (I; X=Y=CH) afforded under the same reaction conditions a mixture, separated by thick layer chromatography giving 82 % of 6-aminoimidazo/1,2-b/pyridazine (II; X=Y=CH), identical in m.p. and ir with an authentical sample prepared according to lit.[5], 1 % of azocompound (IV;X=Y=CH) which was reduced to II (X=Y=CH), 16 % of 6H,13H-diimidazo/1,2-*b*:1',2'-*b'*/pyrazino/2,3-*e*:5,6-*e'*/dipyridazine III (X=Y=CH),/m.p. >350°, ir (KBr) NH 3240 cm^{-1}, nmr (conc.D_2SO_4) τ =1,70 (H_7,H_{14},s), τ = 1,95(H_3,H_{10},s), τ = 2,20 (H_2,H_9,s), high resolution m.s. m/e = 264,08743, calcd.for $C_{12}H_8N_8$ m/e = 264,0871 and ~1 % of polymeric material (m.s. m/e >600).

On the other hand, 6-azidotetrazolo/1,5-*b*/pyridazine[6] (I; X=Y=N) gave 95 % of 6-aminotetrazolo/1,5-*b*/pyridazine (II; X=Y=N), identical with the compound prepared according to lit.[6], 3 % of azocompound (IV; X=Y=N) which was reduced with $Na_2S_2O_4$ to II (X=Y=N) and 2 % of polymeric material (m.s. m/e >600).

A detailed account of this work will be published elsewhere.

REFERENCES

1. T. Sasaki, K. Kanematsu, M. Murata, *J. Org. Chem.*, *36*, 446 (1971)
2. Robert O. Kan, *Organic Photochemistry*, McGraw-Hill, New York, 1966, p.248
3. A. Kovačič, B. Stanovnik, M. Tišler, *J. Heterocyclic Chem.*, *5*, 351 (1968)
4. N. Takahayashi, *J. Pharm.Soc. Japan*, *76*, 765 (1956); *Chem.Abstr.*, *51*, 1192
5. B. Stanovnik, M. Tišler, *Tetrahedron*, *23*, 387 (1967)
6. T. Itai, S. Kamiya, Chem. Pharm. Bull. (Tokyo), *11*, 348 (1963); *Chem.Abstr.*, *59*, 8734 (1963)