Photolysis of 2-Azidopyridine 1-Oxides. A Convenient Synthesis of 1,2-Oxazines

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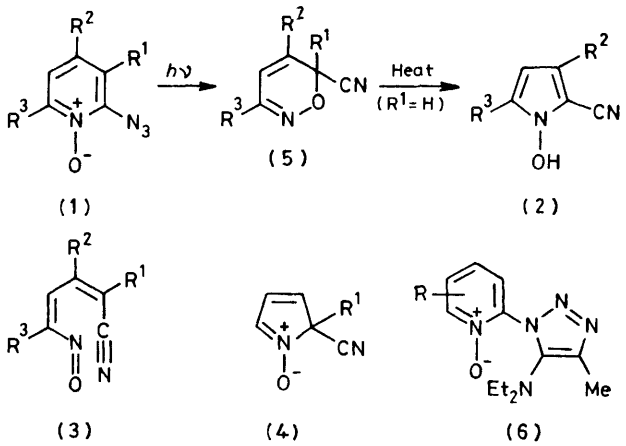
Summary Photolysis or thermolysis of 2-azidopyridine 1-oxides (**1**) in benzene leads to nitrogen-elimination and ring-opening followed by recyclisation to give 6-cyano-1,2-oxazines (**5**) which then usually rearrange thermally to 2-cyano-1-hydroxypyrroles (**2**); the photolyses provide a ready, high-yield route to 1,2-oxazines.

THERMOLYSIS of 2-azidopyridine 1-oxides (**1**; $R^1 = H$) in benzene at 90 °C resulted in an interesting ring contraction and the formation of 2-cyano-1-hydroxypyrroles (**2**).[1] It was proposed that ring-opening concerted with nitrogen elimination gave (**3**) which cyclised to (**2**) *via* a 2-cyano-2*H*-pyrrole 1-oxide. When a 3-methyl group was present formation of a stable 2-cyano-2-methyl-2*H*-pyrrole 1-oxide (**4**) was reported.[1] On the other hand, when a 3-halogeno-substituted (**1**) was used thermolysis gave the 6-cyano-6-halogeno-1,2-oxazine.[2] More recently, a fused benz[*c*]-1,2,5-oxadiazine has been prepared by heating 2-azido-3-methylquinoxaline 1,4-dioxide.[3] In this latter case, it was suggested that the 2*H*-pyrrole was the product of kinetic, and the oxazine that of thermodynamic, control.

It has now been found that photolysis of (**1**) under mild conditions (350 nm; 0·01M benzene solution; room temperature; *ca.* 1 h) gives good yields of the 6-cyano-1,2-oxazines (**5**) [isolated yields: (**5a**), 94%; (**5b**), 96%; (**5c**), 45%;† (**5d**), 70%†]. The oxazines were generally unstable at room

† (**5c**) was formed together with 2-cyano-1-hydroxy-3-methylpyrrole (50%), and (**5d**) together with 2-cyano-1-hydroxy-5-methylpyrrole (21%).



a: $R^1 = R^3 = R^3 = H$
b: $R^1 = Me$; $R^2 = R^3 = H$
c: $R^1 = R^3 = H$; $R^2 = Me$
d: $R^1 = R^2 = H$; $R^3 = Me$

temperature and had to be used soon, or kept at dry-ice temperature under dry nitrogen to prevent polymerisation. In hot toluene they were converted into the *N*-hydroxypyrroles (**2**) (when $R^1 = H$). Structural assignments were based on spectral properties (^1H and ^{13}C n.m.r., i.r., u.v., and mass spectra), and on combustion analyses. Compounds (**5**) absorbed between 275 and 280 nm in the u.v. and exhibited an N–O stretching band between 965 and 950 cm^{-1}.[2] The ^1H n.m.r. spectrum of (**5a**) is typical: δ 7·7 (dd, $J_{3,4}$ 4·0, $J_{3,5}$ 1·5 Hz, 3-H), 5·9 (dd, $J_{4,5}$ 9, $J_{3,4}$ 4·0 Hz, 4-H), 6·1 (ddd, $J_{5,6}$ 5·1 Hz, 5-H), and 5·4 (d, $J_{5,6}$ 5·1 Hz, 6-H). The ^{13}C n.m.r. spectrum exhibited peaks at 148·2, 116·45, 124·2, 59·25, and 115·3 p.p.m. attributed to C-3, C-4, C-5, C-6, and CN, respectively. Assignments were supported by the n.m.r. spectra of methyl-substituted derivatives which also permitted the elimination of isomeric structures such as oxazetine and oxaziridine derivatives.‡ Support for the proposed structure comes from the fact that (**5**) is unreactive towards methyl iodide[6] and dimethyl acetylenedicarboxylate[5] at room temperature.

Compound (**5b**) is identical to the product previously obtained by thermolysis of (**1b**) in boiling toluene to which structure (**4**; R^1 = Me) was incorrectly assigned.[1] The new results clearly establish structure (**5b**) as the correct one. The 1,3-dipolar cycloaddition product formed from (**5b**) and phenyl isocyanate at higher temperatures undoubtedly involves isomerisation of (**5b**) to (**4**). On the other hand, (**5b**) is stable at 90 °C in toluene.

Our results indicate that (**5**) is the product of kinetic and (**2**) the product of thermodynamic control on ring-closure of (**3**), which is the reverse of what has been found in the case of the decomposition of 2-azido-3-methylquinoxaline 1,4-dioxide.[3] This was proved conclusively by the thermolysis of (**1a**) in benzene and following the progress of the reaction both by t.l.c. and by ^1H n.m.r. spectroscopy. After short periods of time (**5a**) appeared as (**1a**) disappeared, reached a maximum concentration, and then started to disappear as well to be replaced by (**2a**) as heating was continued. Thus, both photolysis at room temperature and thermolysis of (**1**) lead to N_2 elimination and ring-opening to (**3**) which then undergoes electrocyclic ring-closure to (**5**). When $R^1 = H$, (**5**) isomerises thermally to (**2**).

In an attempt to trap the open-chain compound the photolysis was carried out at room temperature in the presence of a variety of acetylenes. No product was obtained except with 1-diethylaminopropyne when the thermal 1,3-dipolar cycloadducts (**6**)§ of (**1**) with the ynamine were formed (u.v. irradiation was unnecessary).

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‡ Thus, no bands expected for the protons in α,β-unsaturated nitriles were found,[4] and the presence of the band for 3-H at δ 7·7 eliminates the possibility of its being present in an oxaziridine ring that could have arisen from (**4**) on photolysis.[5]

§ All new products gave expected microanalytical and spectral data.

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