Photolyses of Iminoquinolinium and Iminothiazolium Ylides

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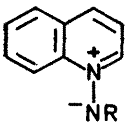
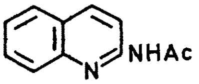
Summary The photolyses of *N*-substituted iminoquinolinium ylides and acetylimino-2,4-dimethylthiazolium ylide mainly gave photofragmentation products.

As compounds isoelectronic with pyridine *N*-oxides,[1] the photolyses of *N*-iminopyridinium ylides have been widely studied.[2–5] The photochemical path of *N*-iminoquinolinium ylide derivatives is of interest as a photolytic ring enlargement analogous to *N*-iminopyridinium ylides would convert the benzenoid ring into a quinonoid structure.

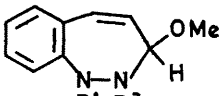
The irradiation through Pyrex of a methanolic solution of acetyliminoquinolinium ylide (I; R = Ac; m.p. 166—167°, λ_{max} 322 nm) gave quinoline (20% yield), methyl methylcarbamate (11% yield), 2-acetylaminoquinoline[6] (II, 6% yield), and a methanol adduct (6% yield), together with a 7% yield of polymeric substances. The methanol adduct was monomeric (mass and Rast) and its n.m.r. spectrum showed, as well as the methyl signals at τ 6·53 and 7·72, a complex multiplet between 2·7—4·5. From these results and the i.r. spectrum (NH at 3290 and C=O at 1660 cm^{-1}), a dihydrobenzo-1,2-diazepine structure (III; R^1 = H, R^2 = Ac, or, less plausibly,[3,4,7] R^1 = Ac, R^2 = H) may tentatively be assigned to this product. Although enough of this compound could not be isolated to permit further characterization, the spectra of the adduct did not agree with dihydrobenzo-1,3-diazepine structures, and the 1-acetylamino-2-methoxy-1,2-dihydroquinoline structure was discounted by spectral comparison with 1-cyano-2-methoxy-1,2-dihydroquinoline.[8] Thus, as for the photolytic behaviour of *o*-substituted iminopyridinium ylides[3,4] and thioureidopyridinium ylides,[5] the main reaction is a photo-Curtius reaction. Another reaction which competes with fragmentation is a valence isomerisation to a condensed diaziridine, which isomerises to (II) and to a benzodiazepine derivative, the latter taking up a molecule of methanol to give adduct (III). (II) may also arise from benzodiazepine.



(I)



(II)



(III)

The photolyses of (I; R = Ac), *N*-benzoyl- (I; R = Bz; m.p. 192—193°) and *N*-tosyl- (I; R = p-Me $C_6H_4\cdot SO_2$; m.p. 227—228°) iminoquinolium ylides in various solvents were also investigated. In all of these cases except the one described above, photo-fragmentation to quinoline and nitrene derivatives was the main reaction path, accompanied by the formation of a variable quantity of polymeric material. In no case, could monomeric isomeric or ring enlargement products be isolated.

The photolysis (low-pressure mercury lamp) of 3-acetylimino-2,4-dimethylthiazolium ylide (m.p. 196—197°; λ_{max} 250 nm) in methanol also afforded a 14·4% yield of 2,4-dimethylthiazole and a 6·4% yield of methyl methylcarbamate as the only isolable products.

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[1] G. G. Spence, E. C. Taylor, and O. Buchardt, *Chem. Rev.*, 1970, **70**, 231.

[2] J. Streith and J. M. Cassal, *Angew. Chem. Internat. Edn.*, 1968, **7**, 129; *Tetrahedron Letters*, 1968, 4541; *Bull. Soc. chim., France*, 1969, 2175.

[3] V. Sniekus, *Chem. Comm.*, 1969, 831; V. Sniekus and G. Kan, *ibid.*, 1970, 172; A. Balasubramanian, J. M. McIntosh, and V. Sniekus, *J. Org. Chem.*, 1970, **35**, 433.

[4] T. Sasaki, K. Kanematsu, and A. Kakehi, *Chem. Comm.*, 1969, 432; T. Sasaki, K. Kanematsu, A. Kakehi, I. Ichikawa, and K. Hayakawa, *J. Org. Chem.*, 1970, **35**, 426.

[5] K. T. Potts and R. Dugas, *Chem. Comm.*, 1970, 732.

[6] T. Nishizawa and H. Shiga, *J. Pharm. Soc. Japan*, 1943, **63**, 441.

[7] C. Kaneko, S. Yamada, I. Yokoe, and T. Kubota, *Tetrahedron Letters*, 1970, 2333.

[7] M. D. Johnson, *J. Chem. Soc.*, 1962, 283.