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FURTHER STUDIES IN THE PHOTOREARRANGEMENT OF HETEROCYCLIC NITROALKENES;[1] A FACILE SYNTHESIS OF 6-HYDROXY-1,2-OXAZINES

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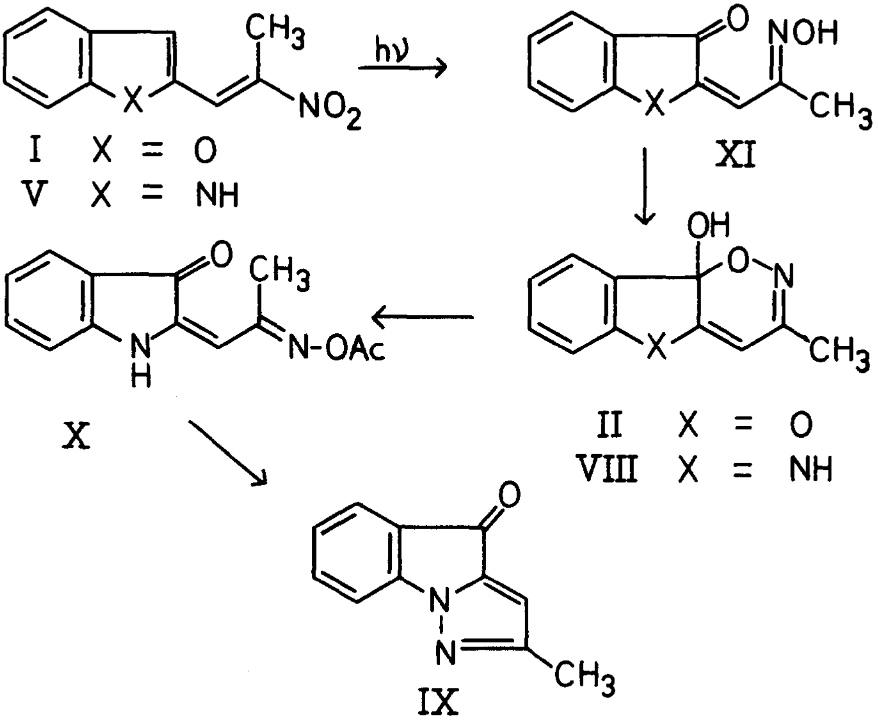
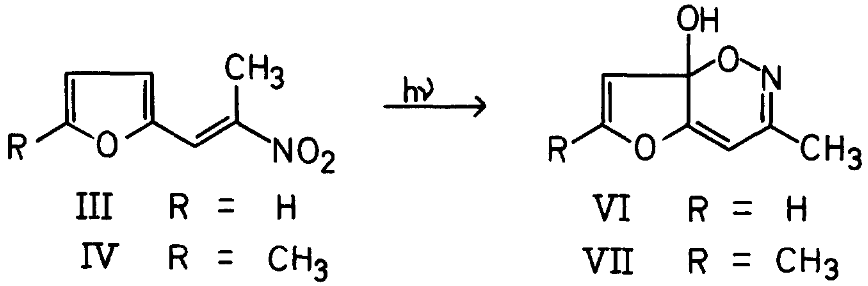
We recently reported the photorearrangement of 3-(2-nitroprop-1-enyl)indole to 3-(2-hydroxyiminopropylidene)-2-oxindole,[2] and speculated that the ease of conversion could at least partly be attributed to the dipolar character of 3-(2-nitroprop-1-enyl)indole. Such character is well-documented for indole-3-aldehyde and related compounds. A study of other heterocyclic nitroalkenes is now reported, and the photoproducts, a series of novel fused 6-hydroxy-1,2-oxazines, are assumed to be formed by an analogous process.

Irradiation of 2-(2-nitroprop-1-enyl)benzofuran (I) in acetone solution (0.01 M) with a medium pressure mercury arc and employing a pyrex filter gave, on removal of the solvent, a crystalline photoproduct (45%) with m.p. 235° from acetone; ν_{max} (nujol) 3320, 1604 and 1581 cm^{-1}. The molecular formula was established as $C_{11}H_9NO_3$ by analysis and mass spectra; m/e 203 (M^+), 187, 186, 175, 146 (loss of C_2H_3NO), 119 and 118. A satisfactory NMR spectrum proved difficult to obtain due to the insolubility and ready decomposition of the photoproduct, but signals at $\delta[(CD_3)_2SO]$ 1.90 (3H, s) and 7.10 (4H, m) were observed; there was no signal characteristic of the C-3 proton of benzofuran.

On this evidence, the photoproduct was assigned the 6-hydroxy-1,2-oxazine structure II. Analogous photorearrangements were observed with

2-(2-nitroprop-1-enyl)furan (III), its 5-methyl derivative (IV), and with 2-(2-nitroprop-1-enyl)indole (V) to give the corresponding oxazines VI, VII and VIII.[3]





The preparation of a number of simple 6-hydroxy-1,2-oxazines by cyclisation of the mono-oxime of 2-alkene-1,4-dione derivatives has previously been reported.[4,5] With a view to further characterising the fused 6-hydroxyl-1,2-oxazine system, we attempted to prepare the 6-acetoxy derivatives of photoproducts II, VI and VIII by the procedure described in the literature for 6-hydroxy-3,4,6-triphenyl-1,2-oxazine.[4] Stable acetates of the oxazines II and VI could not be obtained, but treatment of the oxazine VIII with acetic anhydride led to 2-methyl-4*H*-pyrazolo [1,5-*a*]indol-4-one (IX),[6] m.p. 111-113°, ν_{max} 1722, 1624 and 1600 cm^{-1}, m/e 184,063639 (M^+) and 143 (loss of $CH_3.CN$), $\delta(CCl_4)$ 7.25 (4H, m), 6.2 (1H, s) and 2.35 (3H, 3), formed presumably *via* the oxime acetate X. In solution the 6-hydroxy-1,2-oxazine is considered to be in equilibrium with the acyclic oxime XI which undergoes direct acetylation to form the acetate X. There is, however, no spectral evidence for the existence of an acyclic oxime in the crystalline state in any of these oxazines.

This result prompted us to reinvestigate the product of acetylation of 6-hydroxy-3,4,6-triphenyl-1,2-oxazine. Spectral evidence supported the assignment of the acetoxyimino structure in agreement with our findings rather than the previously reported 6-acetoxy-1,2-oxazine structure.[5] Full details will be reported in our forthcoming paper.

The photorearrangements described here extend our earlier report[2] and indicate that the behaviour now reported is characteristic of the conjugated nitrodiene system in general, although different to that exhibited by the conformationally rigid 6-nitrocholesta-3,5-diene which undergoes rearrangement to 3-hydroxyiminocholest-4-en-6-one.[7] The reaction can in our view best be accounted for in terms of the cyclic process previously described,[2] for which there is ample precedent in the photochromism of certain nitrostyrene derivatives;[8] initial formation of the hydroxyimino-ketone XI by this route is followed by cyclisation to the 1,2-oxazine II.

Attempts to extend this reaction to the acyclic nitrodiene, 4-nitro-1-phenylpenta-1,3-diene, have so far been frustrated by the ready dimerisation of this compound even in dilute solution.[9]

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