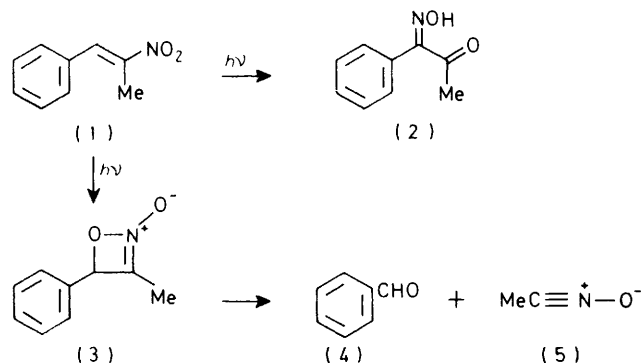


Photochemical Transformations. Part 11.¹ Photorearrangement of 1-(2-Pyridyl)- and 1-(3-Pyridyl)-2-nitropropenes

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Pyrex-filtered irradiation of 1-(2-pyridyl)- and 1-(3-pyridyl)-2-nitropropene in acetone solution gives 1-(2-pyridyl)- and 1-(3-pyridyl)-1-hydroxyimino-propan-2-one, respectively, in high yield.

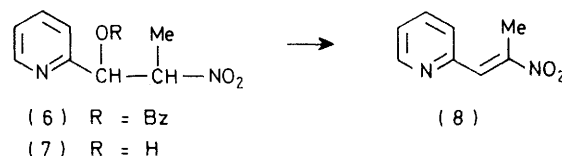
$\alpha\beta$ -UNSATURATED nitroalkenes have been shown to undergo a variety of photoinduced reactions. 2-Nitro-1-phenylpropene (1), on irradiation in acetone, is converted in high yield into 1-hydroxyimino-1-phenylpropan-2-one (2).² Analogous rearrangements have been observed for other 1-aryl-2-nitropropenes. A competing but minor pathway has been described resulting in carbon-carbon double bond cleavage and the formation of the aldehyde (4) and the nitrile oxide (5);³ the *N*-oxide (3) is believed to be an intermediate, and the process is favoured in derivatives containing an electron-withdrawing group.^{3,4} Identical rearrangements to hydroxyimino-ketones have been reported recently in simple aliphatic nitroalkenes⁵ where previously only



double bond migrations and conversion into $\alpha\beta$ -unsaturated ketones had been observed.^{2,6} In contrast, a preliminary investigation has shown that a different process leading to 6-hydroxy-1,2-oxazines occurs on irradiation of 2-(2-nitroprop-1-enyl)furan, 2-(2-nitroprop-1-enyl)benzo[*b*]furan, and 2-(2-nitroprop-1-enyl)indole.⁷ These results prompted us to examine the behaviour of the corresponding pyridyl derivatives in an attempt to define the precise requirements for rearrangement.

2-Nitro-1-(3-pyridyl)propene (9) was prepared by condensation of pyridine-3-carbaldehyde with nitroethane according to the method of Burger and his co-workers.⁸ Under identical conditions, both pyridine-2-

and -4-carbaldehyde react with nitroethane to give the corresponding 1-(2-pyridyl)- and 1-(4-pyridyl)-2-nitropropan-1-ols.⁹ Reported attempts to convert these nitro-alcohols into nitroalkenes using a variety of reagents resulted in the evolution of oxides of nitrogen accompanied by the formation of resinous material.^{8,9}



Accordingly, the benzoate ester (6) of 1-(2-pyridyl)-2-nitropropan-1-ol (7) was prepared with a view to effecting elimination under mild conditions, an approach which has been used in the preparation of simple nitroalkenes.¹⁰ The benzoate (6) was prepared by treatment of the nitro-alcohol (7) with benzoyl chloride in pyridine; crystallisation of the crude benzoate, ν_{\max} 1683 cm^{-1} , gave, not the benzoate, but the required 1-(2-pyridyl)-2-nitropropene (8) directly. The structure was unambiguously established by analytical and spectral data. It was subsequently shown that treatment of the nitro-alcohol (7) with acetyl chloride or acetic anhydride in pyridine or sodium acetate in acetic anhydride gave the acetate, which in turn was converted on heating in cyclohexane or carbon tetrachloride into the nitroalkene (8). Unfortunately attempts to convert the corresponding 1-(4-pyridyl)-2-nitropropan-1-ol into 1-(4-pyridyl)-2-nitropropene *via* the acetate or the benzoate were unsuccessful; a dark red oil was obtained with no spectral evidence for the presence of an $\alpha\beta$ -unsaturated nitro-group.

A solution of 1-(3-pyridyl)-2-nitropropene (9) in acetone was irradiated with a medium-pressure mercury arc through a Pyrex filter until the absorption at 1514 cm^{-1} (NO_2 asym. str.) was no longer present. A crystalline rearrangement product obtained in 81% yield was identified as 1-hydroxyimino-1-(3-pyridyl)propan-2-one (11) on the basis of analytical and spectral

¹ Part X, D. J. Haywood, R. G. Hunt, C. J. Potter, and S. T. Reid, preceding paper.

² O. L. Chapman, P. G. Cleveland, and E. D. Hoganson, *Chem. Comm.*, 1966, 101.

³ I. Saito, M. Takami, and T. Matsuura, *Tetrahedron Letters*, 1975, 3155.

⁴ J. T. Pinhey and E. Rizzardo, *Tetrahedron Letters*, 1973, 4057.

⁵ J. S. Cridland, P. J. Moles, S. T. Reid, and K. T. Taylor, *Tetrahedron Letters*, 1976, 4497.

⁶ J. T. Pinhey and E. Rizzardo, *Chem. Comm.*, 1965, 362; G. E. A. Coombes, J. M. Grady, and S. T. Reid, *Tetrahedron*, 1967, **23**, 1341; G. Descotes, Y. Baharel, M. Bourillot, G. Pingeon, and R. Rostaing, *Bull. Soc. chim. France*, 1970, 290.

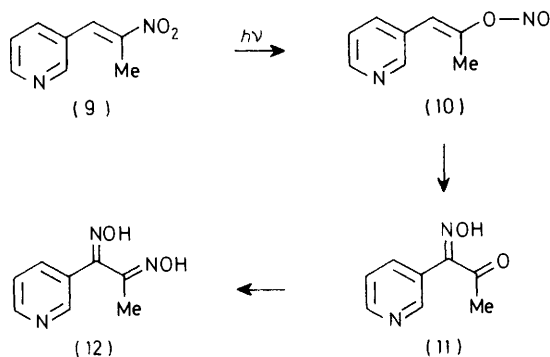
⁷ R. Hunt, S. T. Reid, and K. T. Taylor, *Tetrahedron Letters*, 1972, 2861.

⁸ A. Burger, L. Stein, and J. Clements, *J. Org. Chem.*, 1957, **22**, 143.

⁹ F. Zymalkowski, *Arch. Pharm.*, 1956, **289**, 52.

¹⁰ V. V. Perekalin, 'Unsaturated Nitro Compounds,' Israel Program for Scientific Translations, Jerusalem, 1964.

data and by analogy with the behaviour of the corresponding phenyl derivative. Absorptions at 3 580 and 1 687 cm^{-1} were assigned to O-H and C=O stretching modes, and ^1H n.m.r. signals at δ 2.49 (3 H, s, CH_3), 3.37 (1 H, s, OH), 7.65 (2 H, m, 4- and 5-H), and 8.59 (2 H, m, 2- and 6-H) were consistent with the proposed



structure. The oxime (11) readily affords the dioxime (12) with hydroxylamine.

1-(2-Pyridyl)-2-nitropropene is similarly converted into 1-hydroxyimino-1-(2-pyridyl)propan-2-one in 52% yield by irradiation in acetone. Both rearrangements also occur with methanol as solvent although in lower yield, indicating that acetone does not have an essential role as a triplet sensitizer. Rearrangement presumably occurs *via* the corresponding unsaturated nitrite (10), as previously postulated for 9-nitroanthracene,¹¹ 1-phenyl-1-nitroprop-1-ene,² and 2-nitrofuran and 2-nitropyrrole.¹² Non-co-planarity of the nitro-group and the unsaturated system appears to be a requirement for this rearrangement to occur.¹¹ Thermal or photochemical homolysis of the nitrogen-oxygen bond in the unsaturated nitrite (10) to give an alkoxy radical and NO, followed by radical recombination at C-1, accounts for the formation of the oxime (11).

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. I.r. and u.v. spectra were recorded with a Perkin-Elmer 257 and a Unicam SP 800 spectrophotometer, respectively, and n.m.r. spectra with a Perkin-Elmer R 10 spectrometer (SiMe_4 as reference).

2-Nitro-1-(3-pyridyl)propene (9).—2-Nitro-1-(3-pyridyl)propene, prepared (71%) from pyridine-3-carbaldehyde and

nitroethane by the method of Burger and co-workers,⁸ had m.p. 66–67° (lit.,⁸ 67°), ν_{max} (Nujol) 1 632, 1 590, 1 514, and 1 350 cm^{-1} ; δ (CDCl_3) 2.50 (3 H, s), 7.7 (2 H, m), 8.18 (1 H, s), and 8.82 (2 H, m).

2-Nitro-1-(2-pyridyl)propan-1-ol (7).—Freshly distilled pyridine-2-carbaldehyde and nitroethane in the presence of diethylamine, treated by the method of Zymalkowski,⁹ gave 2-nitro-1-(2-pyridyl)propan-1-ol, m.p. 92° (lit.,⁹ 94°); δ (CDCl_3) 1.45 (3 H, d, J 6 Hz), 4.6 (1 H, s), 5.05 (2 H, m), 7.7 (3 H, m), and 8.8 (1 H, m).

2-Nitro-1-(2-pyridyl)propene (8).—A suspension of 2-nitro-1-(2-pyridyl)propan-1-ol (18.2 g) and anhydrous sodium acetate (10.0 g) in acetic anhydride (50 ml) was stirred at room temperature for 48 h and poured into water (250 ml). The resulting mixture was stirred for 1 h, and the aqueous solution then extracted with chloroform (3 times). The combined extracts were washed with aqueous sodium carbonate and with water, and dried (Na_2SO_4). Removal of the chloroform by distillation and crystallisation of the residue from cyclohexane or carbon tetrachloride gave the 2-nitropropene (4.5 g, 24%), m.p. 76–77° (from ethyl acetate); ν_{max} (CCl_4) 1 665, 1 582, 1 521, and 1 330 cm^{-1} ; δ (CCl_4) 2.79 (3 H, s), 7.9 (4 H, m), and 9.1 (1 H, d) (Found: C, 58.5; H, 4.7; N, 16.9. $\text{C}_8\text{H}_8\text{N}_2\text{O}_2$ requires C, 58.5; H, 4.9; N, 17.1%).

1-Hydroxyimino-1-(3-pyridyl)propan-2-one (11).—A solution of 2-nitro-1-(3-pyridyl)propene (5.0 g) in acetone (600 ml) was irradiated with a medium-pressure mercury arc through a Pyrex filter until the absorption at 1 514 cm^{-1} was no longer detectable. Dry oxygen-free nitrogen was bubbled through the solution for 1 h prior to irradiation and continued throughout. Removal of the acetone by distillation and crystallisation of the residue from methanol gave the ketone, m.p. 203–204° (4.05 g, 81%); ν_{max} (Nujol) 3 160, 1 687, 1 600, and 1 571 cm^{-1} ; δ [$(\text{CD}_3)_2\text{SO}$] 2.49 (3 H, s), 3.37 (1 H, s), 7.65 (2 H, m), and 8.59 (2 H, m) (Found: C, 58.8; H, 5.0; N, 17.1. $\text{C}_8\text{H}_8\text{N}_2\text{O}_2$ requires C, 58.5; H, 4.9; N, 17.1%). The oxime, prepared in 86% yield using hydroxylamine hydrochloride and sodium acetate in aqueous ethanol, had m.p. 228–229° (from methanol); ν_{max} (Nujol) 3 115 and 1 600 cm^{-1} ; δ [$(\text{CD}_3)_2\text{SO}$] 2.12 (3 H, s), 3.50br (2 H), 7.6 (2 H, m), and 8.5 (2 H, m) (Found: C, 53.5; H, 5.3; N, 23.6. $\text{C}_8\text{H}_8\text{N}_3\text{O}_2$ requires C, 53.6; H, 5.0; N, 23.5%).

1-Hydroxyimino-1-(2-pyridyl)propan-2-one.—A solution of 2-nitro-1-(2-pyridyl)propene (2.0 g) in acetone (600 ml) was irradiated as described above until the absorption at 1 521 cm^{-1} was no longer detectable. The ketone (1.04 g, 52%) had m.p. 135–137° (from methanol); ν_{max} (CCl_4) 3 580, 3 060, and 1 692 cm^{-1} ; δ [$(\text{CD}_3)_2\text{CO}$] 2.4 (3 H, s), 7.6 (3 H, m), and 8.6 (1 H, d) (Found: C, 58.7; H, 5.0; N, 17.2. $\text{C}_8\text{H}_8\text{N}_2\text{O}_2$ requires C, 58.5; H, 4.9; N, 17.1%).

¹¹ O. L. Chapman, D. C. Heckert, J. W. Reasoner, and S. P. Thackaberry, *J. Amer. Chem. Soc.*, 1966, **88**, 5550.

¹² R. Hunt and S. T. Reid, *J.C.S. Perkin I*, 1972, 2527.