

Photochemical Transformations. Part VI.¹ The Photorearrangement of 2-Nitrofuran and 2-Nitropyrrole

By R. Hunt and S. T. Reid,* University Chemical Laboratory, The University, Canterbury, Kent

2-Nitrofuran and 2-nitropyrrole are converted on irradiation into the previously unknown 3-hydroxyiminofuran-2(3*H*)-one and 3-hydroxyiminopyrrol-2(3*H*)-one by a process analogous to that reported for the photorearrangement of certain conjugated nitroalkenes. 2-Methyl-5-nitrofuran undergoes an identical rearrangement, whereas 3-methyl-2-nitrofuran is converted into 5-hydroxyimino-3-methylfuran-2(4*H*)-one.

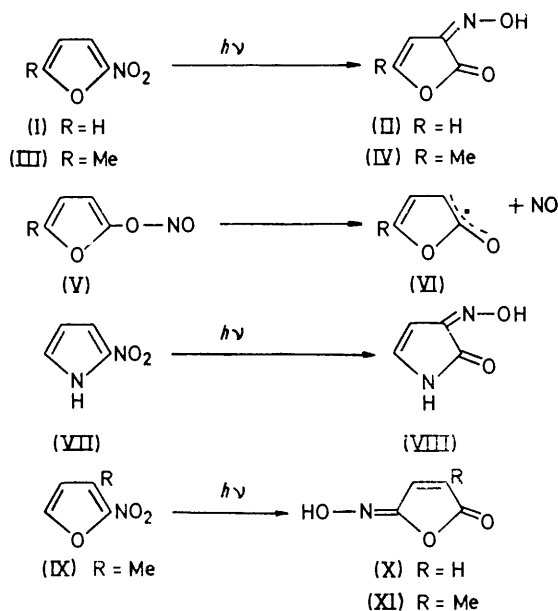
THE solution photochemistry of nitrobenzene has recently attracted considerable attention.² The primary photochemical process is considered to be that of hydrogen abstraction,³ although fragmentation in the vapour phase,⁴ addition to alkenes,⁵ and rearrangement in sterically hindered nitrobenzene derivatives⁶ have also been reported. Hydrogen abstraction occurs either intramolecularly, as in the conversion of *o*-nitrobenzaldehyde into *o*-nitrosobenzoic acid,² or intermolecularly from solvent molecules; abstraction from alcohols,⁷ ethers,⁸ amines,⁸ and saturated hydrocarbons⁹ has been reported, and a variety of reduction products of nitrobenzene have been isolated. Alkoxy-nitroxide radical intermediates, formed in the abstraction process, have been identified by e.s.r. spectroscopy.¹⁰

The photoreduction of 4-nitropyridine in propan-2-ol in the presence of acid¹¹ and of 4-nitropyridine *N*-oxide¹² in ethanol have similarly been interpreted in terms of an initial hydrogen abstraction. There are, however, no reports of the irradiation of five-membered nitro-heteroaromatic systems apart from a preliminary account of the photodecomposition of 2-nitrofuran in propan-2-ol in which hydrogen abstraction followed by ring cleavage is postulated.¹³ Alkoxy-nitroxide radicals attributable to hydrogen abstraction have been detected by e.s.r. in the irradiation of 2-nitrofuran in 2,5-dimethyltetrahydrofuran,¹⁰ but the radical concentration was notably lower than that recorded for nitrobenzene. No spectral evidence for the hydrogen abstraction pathway was obtained in the case of 2-nitropyrrole.¹⁰

We report a study of the photochemistry of 2-nitrofuran, 2-methyl-5-nitrofuran, 3-methyl-2-nitrofuran, and 2-nitropyrrole in which a different reaction pathway is observed.¹⁴

2-Nitrofuran (I) has u.v. absorption maxima at 225 (ϵ 3400) and 315 nm (8100).¹⁵ Irradiation of a solution in acetone with a medium-pressure mercury arc sur-

rounded by a water-cooled Pyrex filter resulted in the gradual disappearance of the asymmetric nitro stretching frequency at 1524 cm⁻¹. An *n*, π^* excited state of the nitro-group is assumed to be involved. A crystalline



photoproduct, C₄H₃NO₃, obtained in 79% yield, was identified as 3-hydroxyiminofuran-2(3*H*)-one (II) rather than the alternative 5-hydroxyimino-2-one (X) on the basis of spectral data. This assignment was confirmed by a study of the irradiation of 2-methyl-5-nitrofuran (III) in acetone; an analogous photorearrangement occurred to give the 3-hydroxyimino-2-one (IV).

The formation of the hydroxyimino-lactones (II) and (IV) is best interpreted in terms of an initial photochemically induced rearrangement to the nitrite (V),

¹ Part V, R. Hunt, S. T. Reid, and K. T. Taylor, *Tetrahedron Letters*, 1972, 2861.

² H. A. Morrison in 'The Chemistry of the Nitro and Nitroso Groups, Part I, ed. H. Feuer, Interscience, New York, 1969, p. 181.

³ R. Hurley and A. C. Testa, *J. Amer. Chem. Soc.*, 1966, **88**, 4330.

⁴ S. Hastings and F. Matsen, *J. Amer. Chem. Soc.*, 1948, **70**, 3514.

⁵ J. L. Charlton and P. de Mayo, *Canad. J. Chem.*, 1968, **46**, 1041.

⁶ Y. Kitaura and T. Matsuura, *Tetrahedron*, 1971, **27**, 1583.

⁷ R. A. Finnegan and D. Knutson, *J. Amer. Chem. Soc.*, 1968, **90**, 1670; W. Trotter and A. C. Testa, *J. Amer. Chem. Soc.*, 1968, **90**, 7044.

⁸ J. A. Barltrop and G. A. Hamilton, *J. Chem. Soc. (C)*, 1968, 1467.

⁹ J. W. Weller and G. A. Hamilton, *Chem. Comm.*, 1970, 1390.

¹⁰ R. B. Sleigh and L. H. Sutcliffe, *Trans. Faraday Soc.*, 1971, **67**, 2195.

¹¹ S. Hashimoto, K. Kano, and K. Ueda, *Tetrahedron Letters*, 1969, 2733.

¹² C. Kaneko, S. Yamada, and I. Yokoe, *Tetrahedron Letters*, 1966, 4729.

¹³ W. Kemula and J. Zawadowska, *Bull. Acad. polon. Sci., Sér. Sci. chim.*, 1969, **17**, 599.

¹⁴ For a preliminary account, see R. Hunt and S. T. Reid, *Chem. Comm.*, 1970, 1576.

¹⁵ R. F. Raffauf, *J. Amer. Chem. Soc.*, 1950, **72**, 753.

as previously described for the photoreactions of 9-nitroanthracene¹⁶ and β -methyl- β -nitrostyrene.¹⁷ The ease of rearrangement in these two systems and the absence of such a reaction in the case of nitrobenzene itself has been rationalised in terms of a requirement of non-planarity between the nitro-group and the unsaturated system;¹⁶ rearrangement of this non-planar species to the oxaziridine is then followed by cleavage of the heterocyclic system to give the nitrite. A similar explanation has been put forward to account for the rearrangement of sterically hindered nitrobenzene derivatives to the corresponding phenols.⁶ 2-Nitrofuran, however, like nitrobenzene would be expected to prefer a planar conformation, and the foregoing explanation does not therefore seem to apply in this case.

Thermal or photochemical homolysis of the unsaturated nitrite (V) to give the furyloxy-radical (VI) and NO, followed by radical recombination at C-3, then accounts for the formation of the products (II) and (IV). The absence of any 5-hydroxyimino-product is not surprising in view of the reported photorearrangement of 2-methoxyfuran to 3-methylfuran-2(3*H*)-one,¹⁸ a process which presumably occurs *via* the same intermediate radical.

The photoreaction of 2-nitrofuran was also studied in methanol and a lower yield of the oxime (II) was obtained. In this case, hydrogen abstraction from the solvent, a process which does not appear to be a major pathway in acetone, may well compete with rearrangement; no products arising from such an abstraction were isolated.

An analogous reaction was observed with 2-nitropyrrole (VII); irradiation in acetone gave a 15% yield of 3-hydroxyiminopyrrol-2(3*H*)-one (VIII).

We have also studied the photochemistry of 3-methyl-2-nitrofuran (IX), in which radical recombination at C-3 is less favourable. Irradiation in acetone solution gave 5-hydroxyimino-3-methylfuran-2(5*H*)-one (XI). In this case, radical recombination must occur at C-5. Precedence for this process, in which 2-nitrofuran behaves as a conjugated nitro-diene, is to be found in the photorearrangement of 6-nitrocholesta-3,5-diene to 3-hydroxyiminocholest-4-en-6-one.^{17,19}

EXPERIMENTAL

Photolyses were carried out with a Hanovia 1 l photochemical reactor fitted with a 100 W medium-pressure mercury arc surrounded by a water-cooled quartz jacket.

¹⁶ O. L. Chapman, D. C. Heckert, J. W. Reasoner, and S. P. Thackaberry, *J. Amer. Chem. Soc.*, 1966, **88**, 5550.

¹⁷ O. L. Chapman, P. G. Cleveland, and E. D. Hoganson, *Chem. Comm.*, 1966, 101.

¹⁸ R. Srinivasan and H. Hiraoka, *Tetrahedron Letters*, 1969, 2767.

Dry, oxygen-free nitrogen was bubbled through the solutions for 1 h prior to irradiation, and oxygen was excluded during the experiment. The progress of a reaction was followed by observing the reduction in intensity of the i.r. band due to the asymmetric stretching of the nitro-group (around 1520 cm⁻¹).

M.p.s were determined with a Kofler hot-stage apparatus. I.r. spectra were recorded on a Perkin-Elmer 237 or 257 spectrometer and n.m.r. spectra on a Perkin-Elmer R10 spectrometer with tetramethylsilane as reference.

3-Hydroxyimino-furan-2(3*H*)-one (II).—A solution of 2-nitrofuran²⁰ (5.0 g) in acetone (1 l) was irradiated until the i.r. band at 1524 cm⁻¹ was no longer detectable. Removal of the solvent by distillation and crystallisation of the product from methanol gave the *furanone* (II) (3.8 g, 79%), m.p. 132°, ν_{\max} (CH₂Cl₂) 3539, 1804, 1659, 1322, 1103, 1063, 990, 930, 862, and 819 cm⁻¹, τ [(CD₃)₂CO] 6.8br (1H), 3.45 (1H, d, *J* 5 Hz, H-4), and 2.44 (1H, d, *J* 5 Hz, H-5), λ_{\max} 276 nm (ϵ 11,300) (Found: C, 42.7; H, 2.8; N, 12.5. C₄H₅NO₃ requires C, 42.5; H, 2.7; N, 12.4%).

3-Hydroxyimino-5-methylfuran-2(3*H*)-one (IV).—2-Methyl-5-nitrofuran²¹ (2.0 g) in acetone (600 ml) was irradiated as described for 2-nitrofuran. The acetone was removed by distillation under reduced pressure to yield an oil which after chromatography on silica gel gave white crystals of the *furanone* (IV) (0.64 g, 32%), m.p. 122° (from methanol), ν_{\max} (CH₂Cl₂) 3530, 1808, 1648, 1618, 1380, 1157, 1049, 1009, 965, and 927 cm⁻¹, τ [(CD₃)₂CO] 7.79 (3H, d, *J* 2 Hz), 6.92 (1H, s), and 3.74 (1H, d, *J* 2 Hz), λ_{\max} 235 (ϵ 21,900) and 304 nm (10,200) (Found: C, 47.4; H, 3.9; N, 10.8. C₅H₅NO₃ requires C, 47.2; H, 4.0; N, 11.0%).

5-Hydroxyimino-3-methylfuran-2(5*H*)-one (XI).—A solution of 3-methyl-2-nitrofuran²² (1.0 g) in acetone (600 ml) was irradiated as for 2-nitrofuran. Removal of the solvent by distillation and crystallisation from methanol gave the *furanone* (XI) (0.45 g, 45%), m.p. 114–115°, ν_{\max} (CH₂Cl₂) 3555, 2935, 2860, 1800, 1666, 1634, 1173, 1042, 1019, 956, and 873 cm⁻¹, τ [(CD₃)₂CO] 8.55 (3H, s), 3.35 (1H, s), and -0.1br (1H), λ_{\max} 275 nm (ϵ 1360) (Found: C, 47.1; H, 4.0; N, 11.0. C₅H₅NO₃ requires C, 47.2; H, 4.0; N, 11.0%).

3-Hydroxyiminopyrrol-2(3*H*)-one (VIII).—A solution of 2-nitropyrrole²³ (2.0 g) in acetone (1 l) was irradiated until the i.r. band at 1503 cm⁻¹ was no longer detectable. Removal of the acetone by distillation under reduced pressure gave an oil; chromatography on silica gel gave white crystals of *pyrrolone* (VIII) (0.3 g, 15%), m.p. 210° (decomp.) (from methanol), ν_{\max} (Nujol), 3200, 1680, 1640, 1325, 1210, 1077, 1002, 916, 816, and 720 cm⁻¹, τ [(CD₃)₂SO] 6.7 (1H, s), 3.65 (1H, d, *J* 6 Hz), 2.80 (1H, d, *J* 6 Hz), and -0.8br (1H), λ_{\max} 287 nm (ϵ 14,000) (Found: C, 42.6; H, 3.5; N, 25.2. C₄H₄N₂O₂ requires C, 42.9; H, 3.6; N, 25.0%).

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