Tetrahedron Letters,Vol.24,No.21,pp 2209-2210,1983 0040-4039/83/212209-02$03.00/0
Printed in Great Britain

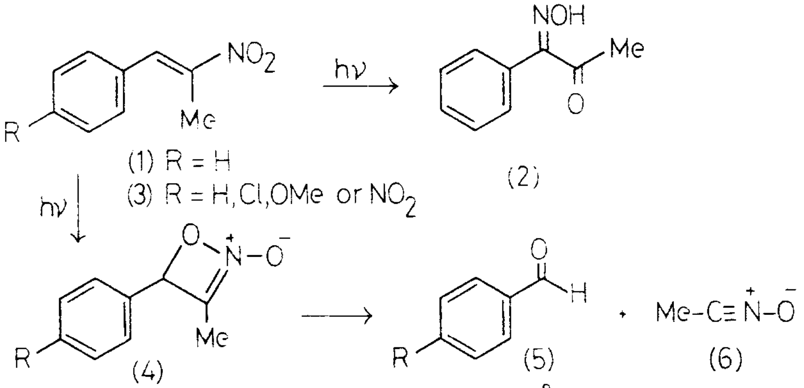
A NOVEL PHOTOREACTION OF 3-NITRO-2-PHENYL-2H-CHROMENE IN METHANOL.[1]

Stewart T. Reid, Julian K. Thompson and (in part) Christopher F. Mushambi
The Chemical Laboratory, The University, Canterbury, Kent. CT2 7NH.

3-Nitro-2-phenyl-2H-chromene (7) is reported to undergo a novel high-yield photoreaction in methanol to give 3-hydroxyimino-4,4-dimethoxy-2-phenylchroman (8).

Various αβ-unsaturated nitroalkenes have been reported to undergo photochemically-induced rearrangement to isomeric α-oximino ketones. The first example of this conversion was described for 1-phenyl-2-nitroprop-1-ene (1) which, on irradiation in acetone, gave the oxime (2) in 81% yield.[2] Analogous rearrangements have since been reported in aryl-substituted 1-phenyl-2-nitroprop-1-enes,[3] in 1-(2-pyridyl)- and 1-(3-pyridyl)-2-nitroprop-1-enes,[4] in 2-nitrofurans,[5] and in simple acyclic nitroalkenes.[6] A competing but minor fragmentation process has been observed in certain 1-phenyl-2-nitroprop-1-enes (3)[3] and in 2-nitro-1-(9-phenanthryl)prop-1-ene[7] leading to the formation of the corresponding aldehydes; initial photocyclization to oxazete N-oxides (4), followed by cleavage to the aldehydes (5) and the nitrile oxide (6) which has been trapped as an isoxazoline with methyl acrylate, has been proposed to account for these transformations.

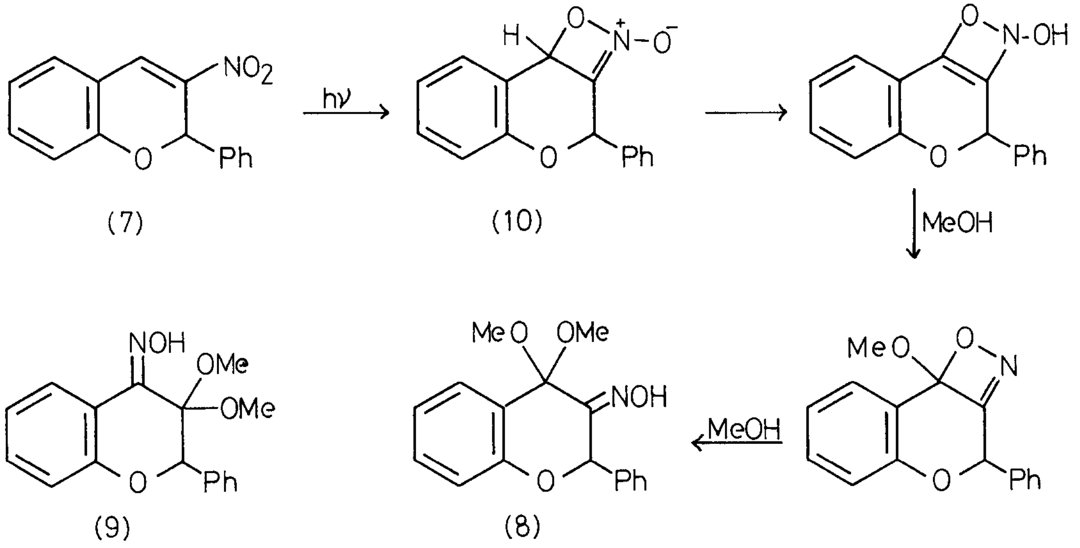
In this paper, we report a novel high-yield photoreaction of 3-nitro-2-phenyl-2H-chromene which we believe is related to this cyclization.



A 0.008 M solution of 2-phenyl-3-nitro-2H-chromene[8] (7) was irradiated in methanol solution through Pyrex with a 450 w medium pressure mercury arc until absorption at 1510 cm^{-1} in the infrared was no longer present. Distillation of the solvent and crystallization of the resulting oil from toluene gave in 79% yield a photoproduct, m.p. 176-178°C, with ν_{max} (CH_2Cl_2) 3540, 3300, 1610 and 1590 cm^{-1}, and δ_H ($CDCl_3$) 3.10 (3H,s), 3.62 (3H,s), 5.43 (1H,s) 7.0-7.6 (9H,m) and 8.2 (1H,br) ppm. Analytical and mass spectral data, m/e 299 (M^+), support a molecular formula of $C_{17}H_{17}NO_4$. Two isomeric structures, (8) and (9), satisfy these observations. Ultraviolet absorptions of λ_{max} 231 (ε 4425) and 275 (ε 2875) nm, at shorter wavelengths than those recorded for 4-hydroxyimino-2-phenylchroman (flavanone oxime),[9] λ_{max} 304 (ε 8800) and 313 (ε 7400) nm, support the assignment of structure (8) to the photoproduct.

This assignment was confirmed by hydrolysis of the ketal in (8) with trifluoroacetic acid at 0^{o}C to give the corresponding oximino ketone, m.p. 179-182, ν_{max} (CH_2Cl_2) 3590, 1700 and 1600 cm^{-1}, identical with values previously reported.[10] Furthermore, oxidation of the oximino ketone with alkaline hydrogen peroxide or of photoproduct (8) with sodium hypobromite gave the same nitro ketone, m.p. 137-138^{o}C (lit.[11] 136-138^{o}C), ν_{max} 1705, 1560 and 1370 cm^{-1}, identical in all respects with a sample prepared by oxidation of 4-hydroxy-3-nitro-2-phenylchroman[8] with chromium trioxide in acetic acid.

This novel transformation is best explained in terms of initial photocyclization to the oxazete (10), followed by addition of methanol, as shown below. If the proposal is correct, then this is the first photoreaction reported for αβ-unsaturated nitro compounds in which such a cyclization is the principal reaction pathway. The possibility of the corresponding nitro ketone or the oximino ketone being intermediates in this conversion has been excluded.



References

1. Photochemical Transformations, Part 15. For Part 14, see S.T.Reid and D. De Silva, Tetrahedron Lett., 1983,
2. O.L.Chapman, P.G.Cleveland and E.D.Hoganson, Chem.Commun., 1966, 101
3. I.Saito, M.Takami and T.Matsuura, Tetrahedron Lett., 1975, 3155
4. R.G.Hunt and S.T.Reid, J.Chem.Soc., Perkin Trans. 1, 1977, 2462
5. R.Hunt and S.T.Reid, J.Chem.Soc., Perkin Trans. 1, 1972, 2527
6. J.S.Cridland, P.J.Moles, S.T.Reid and K.T.Taylor, Tetrahedron Lett., 1976, 4497
7. R.A.Humphry-Baker, K.Salisbury and G.P.Wood, J.Chem.Soc., Perkin Trans. 2, 1978, 659
8. T.Sakakibara, M.Koezuka and R.Sudoh, Bull.Chem.Soc.Jpn., 1978, 51, 3095
9. R.Bognor and M.Râkon, Tetrahedron, 1962, 18, 135
10. T.Oyamada and F.Fukawa, J.Chem.Soc.Jpn., 1943, 64, 331
11. M.Michalska, Bull.Acad.Pol.Sci., 1968, 16, 567

(Received in UK 24 February 1983)