

1. Náhlovská, Z., Náhlovský, B. and Strand, T. G. *Acta Chem. Scand.* **24** (1970) 2617.
2. Cyvin, S. J., Alfheim, I. and Hagen, G. *To be published.*
3. Alfheim, I. and Cyvin, S. J. *To be published.*
4. Murata, H. and Kawai, K. *J. Chem. Phys.* **25** (1956) 589.
5. Pava, B. M. and Stafford, F. E. *J. Phys. Chem.* **72** (1968) 4628.
6. Jensen, H. H., Hagen, G. and Cyvin, S. J. *J. Mol. Structure* **4** (1969) 51.

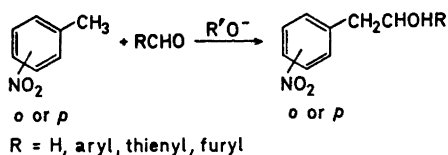
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The Photocyclization of 2-(*o*-Nitrophenyl)-ethanol to *N*-Hydroxyoxindole

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A facile method for the addition of *o*- and *p*-mononitrotoluenes to aldehydes has been reported.¹ By that method, 2-(nitro-aryl)-ethanols became available free from the isomers.

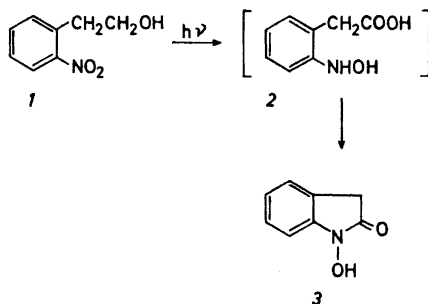


We have studied the chemistry of some of these ethanols.² The present communication will deal with a photochemical reaction of 2-(*o*-nitrophenyl)-ethanol (*1*). The irradiation of 2-(*o*-nitrophenyl)-ethanol in ethanol gave an acidic, crystalline product. IR spectroscopy showed the compound

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to contain a carbonyl group (1685 cm^{-1}), a strongly hydrogen bonded hydrogen atom (broad band from 3200 to 2500 cm^{-1}) and no nitro group.

The oxidising power of the photo-excited nitro group is well known.^{3,4} Oxidation of the hydroxyl group in compound *1* by the nitro group would hypothetically give 2-(*o*-hydroxylaminophenyl)-acetic acid (*2*) which could cyclize to *N*-hydroxyoxindole (*3*):



The product, purified by chromatography and recrystallisation, had IR, m.p., and mixed m.p. (both 199 – 200°) identical to those of an authentic sample⁵ of *N*-hydroxyoxindole.

The degree of conversion 2-(*o*-nitrophenyl)-ethanol as well as the yield of *N*-hydroxyoxindole was influenced by the starting concentration of *1*. They were, however, not influenced by solvent or by the UV light being filtered through pyrex glass, as will be seen from Table 1. The exclusion of oxygen was without effect, and no reaction of compound *1* could be detected by refluxing it in ethanol for 24 h.

During the reaction the solution turned brown. The lowering of the conversion at higher starting concentrations of *1* was probably due to a faster formation of the brown coloured material absorbing the light.

The photochemical redox reaction of 2-(*o*-nitrophenyl)-ethanol was tried under basic condition. If the coloured material was formed by condensation of carboxylic acids with other groups, one could hope that condensation during the irradiation in basic solution might be avoided, thus producing a higher conversion of 2-(*o*-nitrophenyl)-ethanol. However, basic conditions did not give any higher conversion than neutral ones (Table 1).

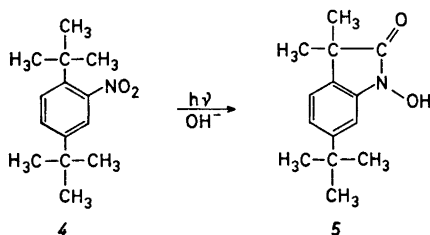
Table 1. Irradiation of 2-(*o*-nitrophenyl)-ethanol (ONPE) with a medium pressure mercury arc (Q 81 Quartzlampen Gesellschaft GmbH), temp. 35°.

Solvent	Starting concentration ONPE, mmole/l	Light source mantle	Reaction time, h	% reacted ONPE ^a	<i>N</i> -Hydroxyoxindole formed, ^b % of reacted ONPE
Benzene	285	Quartz	3.5	27	15
2-Propanol	285	»	3.5	28	17
Ethanol, 95 %	285	»	3.5	25	16
»	86	»	3.5	50	35
»	86	Pyrex	3.5	53	38
Ethanol, 95 % under N ₂	86	»	3.5	48	36
Ethanol, 95 %, 0.07 M NaOH	60	Quartz	5	34	14

^a Unreacted 2-(*o*-nitrophenyl)-ethanol determined by GLC (internal standard method).

^b Isolated by chromatography on silica gel, eluted with CHCl₃, m.p. 190–195°, lit. 199–201°.⁶

Dopp⁷ recently reported the photochemical cyclization of 1-nitro-2,5-di-*t*-butylbenzene (**4**) under basic conditions:



The product, a substituted *N*-hydroxyoxindole (**5**) shows at least one intermolecular oxidation to have taken place. An intramolecular redox process would result in the equivalent of a hydroxylamino group and an aldehyde group, giving an oxindole on cyclization.

Finally, an attempt was made to obtain oxindole or hydroxyoxindole by illumination of *o*-nitroethylbenzene by analogy with Dopp's⁷ experiment. Only 15% of *o*-nitroethylbenzene reacted, and no oxindole, 1-hydroxyoxindole, or other

products could be isolated. The success of Dopp's experiment may be due to the steric requirements of the *t*-butyl group, forcing the methyl groups into close proximity with the nitro group.

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1. Bakke, J. *Acta Chem. Scand.* **21** (1967) 1967.
2. Bakke, J. *Acta Chem. Scand.* **23** (1969) 3055.
3. Calvert, J. G. and Pitts, J. N. *Photochemistry*, Wiley, New York 1966, p. 477.
4. Morrison, H. A. In Feuer, H. *The chemistry of the nitro and nitroso groups*, Interscience, New York 1969, Part 1.
5. Reissert, A. *Ber.* **41** (1908) 3921.
6. Wright, Jr., W. B. and Collins, K. H. *J. Am. Chem. Soc.* **78** (1956) 221.
7. Dopp, D. *Chem. Commun.* **1968** 1284.

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