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STRUCTURE ELUCIDATION OF THE PHOTOLYSIS PRODUCT OF 2,3-DIMETHOXY-5-NITRO-NAPHTHALENE* BY APPLICATION OF N.O.E.**

J. Lugtenburg and E. Havinga
(Department of Organic Chemistry, The University, Post-box 75, Leiden, The Netherlands).

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Application of the intramolecular nuclear Overhauser effect (N.O.E.) to elucidate structural problems have recently been reported [1-3]. In this paper the use of N.O.E. is described for the structure determination of a hitherto unknown compound, originating from irradiation (high pressure Hg-arc) of 2,3-dimethoxy-5-nitronaphthalene in alkaline solution, which has one methyl group less than the parent compound. Two possibilities present themselves for the structure of the photoproduct from previous photochemical experience[4]:

A. 2-hydroxy-3-methoxy-5-nitronaphthalene
B. 2-methoxy-3-hydroxy-5-nitronaphthalene

On the basis of mass-, infrared- and NMR-spectra it is impossible to decide which structure should be assigned to the photoproduct. The UV-spectrum favours structure A.

A 10% solution of the photoproduct in acetonitrile was degassed. The NMR-spectrum showed the following signals:

δ (ppm)	structure	intensity	assignment
2.0	broad singlet		solvent
3.90	singlet	3	CH_3-O
7.16	singlet	1	C_1-H
7.75	singlet	1	C_4-H
7.23	triplet	1	C_7-H
~8.0	multiplet	2	C_6-H + C_8-H

The O-H signal could not be traced.

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* G.M.J. Beijersbergen van Henegouwen, Dissertation, Leiden, to be published.

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When the CH_3-O protons were saturated, the area of the signal for the proton C_4-H increased by 21%; the other peaks were unaffected. Saturation of the C_4-H proton resulted in a 7% increase in the area for the CH_3-O protons. Saturating other peaks did not affect the intensity of the CH_3-O signal.

From these findings it follows that the photoproduct has structure A: 2-hydroxy-3-methoxy-5-nitronaphthalene.

The NMR spectrum of the parent compound 2,3-dimethoxy-5-nitronaphthalene (cf. 3,4) was also investigated. A solution of this compound in acetonitrile was degassed:

δ(ppm)	structure	intensity	assignment
2.0	broad singlet		solvent
3.92	singlet	6	CH_3-O
7.31	singlet	1	C_1-H
7.84	singlet	1	C_4-H
7.37	triplet	1	C_7-H
~8.0	multiplet	2	C_6-H + C_8-H

Saturation of the methoxy signal gave a 27% increase of the C_1-H area and a 36% increase of the C_4-H signal, the other peaks were not affected. Saturation of the C_1-H signal resulted in a 4% increase of the CH_3-O signal. This signal increased by 6% on saturation of the C_4-H signal.

The NMR spectra were run on a Varian HA-100 NMR-spectrometer with TMS as internal lock. For the double resonance measurements a Muirhead Decade Oscillator was used.

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