

PHOTOREACTIONS OF AROMATIC COMPOUNDS¹ XXXII
 FLUORINE AS A LEAVING GROUP IN NUCLEOPHILIC PHOTOSUBSTITUTION REACTIONS OF SOME
 NITRONAPHTHALENE DERIVATIVES²

J.G.Lammers and J.Lugtenburg

Gorlaeus Laboratories, Department of Organic Chemistry, University of Leiden,

P.O. Box 75, Leiden, the Netherlands.

(Received in UK 16 March 1973; accepted for publication 6 April 1973)

We wish to report photoreactions of a few fluoronitronaphthalenes. Nitronaphthalenes are better phosphorescers than nitrobenzenes³, thus providing additional possibility of obtaining information about the excited state.

Irradiation at room temperature of 1-fluoro-3-nitronaphthalene (I) in a solution containing nucleophiles resulted in a clean reaction. Only the product in which fluorine is substituted by the nucleophile is formed (Figure I); isolated yields are 80-90 %. The quantum yield of the reaction in 0.1 N NaOH is 0.33 ($\lambda = 366 \text{ nm}$, solvent $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ 1:1). This reaction can be quenched completely by addition of 3,3,4,4-tetramethyldiazetinedioxide⁴; sensitization by benzophenone is very efficient. The intersystem crossing quantum yield of I is considered to be very high (cf. $\phi_{\text{isc}} = 0.83$ for the related 2-nitronaphthalene³). These data are good indications that the reactions of I start from a triplet state. I is thermally completely stable in the presence of nucleophiles.

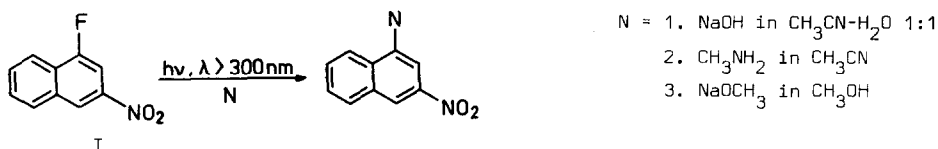


Figure I. Photosubstitution reactions of 1-fluoro-3-nitronaphthalene.

To be able to study the concomitant phosphorescence and photochemical phenomena, I was irradiated at 77° K in a glass of 2-methyltetrahydrofuran (2MTHF) containing 3 M methylamine. A photoreaction is observed under these conditions; after work up at room temperature 1-N-methylamino-3-nitronaphthalene appears to be the reaction product. The addition of 3 M methylamine to the 2MTHF-glass does not change absorption - nor phosphorescence spectra at 77° K. Without methylamine added to the glass, there is only a slow photodecomposition of I.

For comparison the photoreactions of 1-fluoro-4-nitronaphthalene (II), 1-chloro-2-fluoro-4-nitronaphthalene (III) and 1-methoxy-2-fluoro-4-nitronaphthalene (IV) at room temperature were investigated:

II with OH^- gives 1-hydroxy-4-nitronaphthalene as the photoproduct; with CN^- or OCH_3^- the nitro-group is photosubstituted*.

III yields 1-chloro-2-methoxy-4-nitronaphthalene as the main product upon irradiation in the presence of OCH_3^- , while also some 1-chloro-2-fluoro-4-methoxynaphthalene is formed. Use of OH^- in this case results in 1-chloro-2-hydroxy-4-nitronaphthalene in low yield.

In the case of IV each of the substituents can be replaced by nucleophiles:

OH^- gives 1-hydroxy-2-fluoro-4-nitronaphthalene

OCH_3^- gives 1,2-dimethoxy-4-nitronaphthalene and

CN^- gives 1-methoxy-2-fluoro-4-cyanonaphthalene.

As the group which is substituted varies with the nucleophile, it appears that the charge distribution in the excited state is not the sole factor determining the position at which reaction occurs.

There is no indication of thermal reactions with nucleophiles during the irradiation of these compounds. By boiling the compounds in solutions containing OH^- or OCH_3^- ions, a clean reaction is observed in which the group para relative to the nitrogroup is substituted.

Experimental details

Irradiations were carried out with a Hanau TQ 81 lamp in pyrex apparatus ($\lambda > 300 \text{ nm}$). Solutions contained 10-40 mg naphthalene derivative per litre solvent; the temperature was kept at 20-25 $^\circ$ C during the irradiations. The concentrations of nucleophile were 0.1 M (NaOH and CH_3NH_2 in $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ 1:1, KCN in $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ 9:1 and NaOCH_3 in CH_3OH). After acidification of the irradiated solutions the photoproducts were isolated and separated by column chromatography (silicagel, benzene/hexane). The photoproducts were identified by comparison with authentic samples (UV, NMR, IR) and, in cases of unknown compounds, by mass spectrometry and NMR.

Reactions at 77 $^\circ$ K: commercial 2-methyltetrahydrofuran was purified by refluxing over KOH pellets and distillation. Methylamine was distilled prior to use. The 2MTHF-glass was irradiated in pyrex apparatus with a Xenon lamp.

*The substitution of an α -nitrogroup by cyanide or methoxide is a well established photoreaction in the naphthalene series^{5,6}.

Literature

1. Part XXXI: J. den Heijer, T. Spee, G.P. de Gunst and J. Cornelisse, Tetrahedron Letters, 1973, in the press.
2. P. Brasem, J.G. Lammers, J. Cornelisse, J. Lugtenburg and E. Havinga, Tetrahedron Letters, 685 (1972).
3. R. Rusakowicz and A.C. Testa, Spectrochim. Acta 27A, 787 (1971).
4. E. Ullmann and P. Singh, J. Am. Chem. Soc. 94, 5077 (1972).
5. C.M. Lok, J. Lugtenburg, J. Cornelisse and E. Havinga, Tetrahedron Letters, 4701 (1970).
6. R.L. Letsinger and R.R. Hautala, Tetrahedron Letters, 4205 (1969).

Acknowledgement

The authors wish to thank prof. dr. E. Havinga and dr. J. Cornelisse for valuable discussions and mr. K. Batist for experimental assistance. The investigations were supported by the Netherlands Foundation of Chemical Research (S.O.N.) with financial aid from the Netherlands Organisation for the Advancement of Pure Research (Z.W.O.).