Tetrahedron Letters No. 15, pp 1273 - 1276, 1978. Pergamon Press. Printed in Great Britain.

THE PHOTO-SMILES REARRANGEMENT

Kiyoshi Mutai,* Sei-ichiro Kanno, and Keiji Kobayashi
Department of Chemistry, College of General Education
University of Tokyo, Komaba, Meguro, Tokyo 153, Japan

(Received in Japan 14 January 1978; received in UK for publication 21 February 1978)

The Smiles rearrangement is an intramolecular nucleophilic substitution at an aromatic ring, usually catalyzed by base.[1] A photorearrangement yielding the same products as expected from the base-catalyzed reaction may well be called the photo-Smiles rearrangement. We report an example of the photo-Smiles rearrangement.

Recently the various examples of *intermolecular* nucleophilic photosubstitution have been accumulating.[2] The observed facts suggest the possible occurrence of the *intramolecular* reaction, i.e. the photo-Smiles rearrangement, if the appropriate structural conditions for the substrate are provided. It is also interesting to know whether the similar reaction mechanism should operate in both cases. For this purpose we chose a homologous series of *N*-[ω-(p-nitrophenoxy)-alkyl]anilines, **1**. These compounds undergo the Smiles rearrangement in the presence of a base such as NaH or NaOEt to yield **2**. They are stable in neutral solvents.[3]

(1)

1, n=2 ~ 5

2

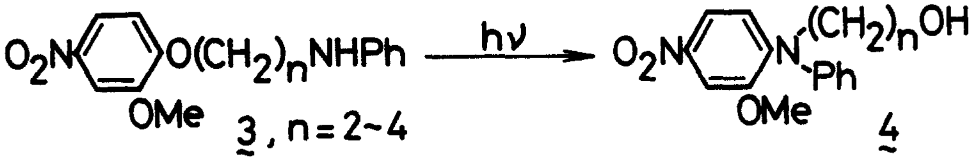
Experimental conditions

A solution of **1**, *ca*. 1×10^{-4} M in concentration, was irradiated with a 100W high-pressure mercury lamp through both Pyrex filter and an aqueous NiSO$_4$ solution of *ca*. 1 cm in pathlength. Thus, practically the exciting light of 313 nm was used for the irradiation. For the determination of the reaction rate, the solution was circulated through a flow cell set in a uv spectrophotometer with which the time dependence of the characteristic absorbance of the product at *ca*. 400 nm was recorded. A more concentrated solution was used for the isolation and identification of the products.

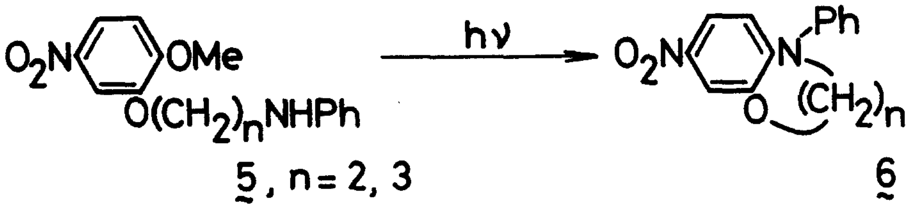
The major products of the photorearrangement in acetonitrile or methanol were easily identified as N-(ω-hydroxyalkyl)-p-nitrodiphenylamines (2) by comparing their spectral data with those of the products obtained by the base-catalyzed rearrangement. Practically complete conversion of 1 to 2 was observed for n=2, 3, and 4.

In *intermolecular* photosubstitution, an interesting meta-favorable orienting feature of nitro group was observed. For instance, 3,4-dimethoxynitrobenzene was irradiated in the presence of methylamine. The products isolated were 3-(methylamino)-4-methoxy- and 3-methoxy-4-(methylamino)nitrobenzenes, and the ratio between the two isomers was 9:1,[4] indicating the predominance of meta substitution.

In order to asses this meta-para activating ability of nitro group in the *intramolecular* case, 3 and 5 were subjected to the photoreaction. The products isolated were 4 from 3 and 6 from 5. No product indicating the meta substitution was detected in the reaction mixtures. The fact that the substitution occurred only at the para position suggests a clue to elucidate the mechanism of the reaction.



(2)



(3)

The *intermolecular* reaction has been interpreted as initiated by the excitation of nitrobenzene derivative. The meta orientation of nitro group has been attributed to the different π-electron distribution in the excited state from that in the ground state.[5,6] In the present study, however, the products (4 and 6) are the same as those expected from the Smiles rearrangement in the dark. Therefore, the intermediates in the reactions (2) and (3), and probably in (1), may be the same as or have closely similar structures to those in the base-catalyzed reactions. In this connection, three experimental facts are cited: (1) N-Methyl derivatives of 1 underwent no photorearrangement. (2) No rearranged product was observed when cyclohexane was used as a solvent. (3) An addition of triethylamine to the solution produced an enhancement of the photoreaction rate as shown in the Table. The amine was ineffective to catalyze the rearrangement without light.

Table

Effect of Et_3N on the relative rate of the photo-Smiles rearrangement of $p\text{-}O_2NC_6H_4O(CH_2)_3NHPh$

	Concentration of Et_3N in CH_3CN (M)			
	0	0.0286	0.143	0.357
Rel. k	1.0	6.4	11	11

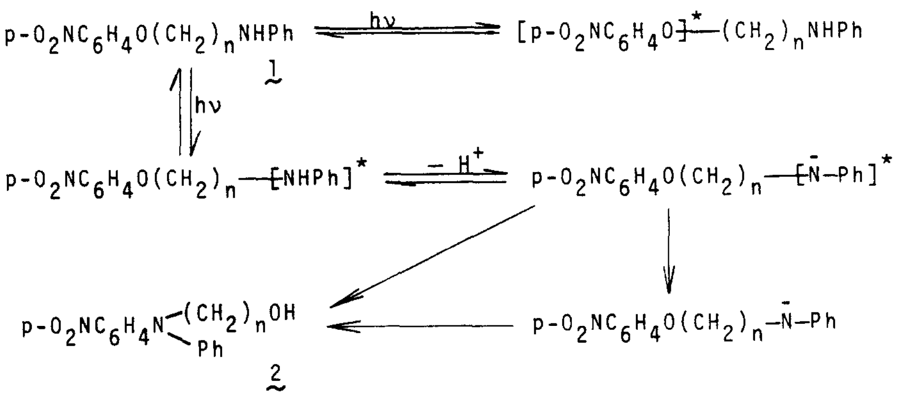
	Concentration of Et_3N in CH_3OH (M)			
	0	0.0286	0.143	0.286
Rel. k	1.0	26	78	98

The fact (1) suggests that the N-H hydrogen is essential for the reaction, and (2) and (3) may be best interpreted as indicating the involvement of an ionic precess, that is, a proton transfer from the substrate to a solvent molecule or an added base.

It has been reported that the acidity of phenols and naphthols increases on excitation,[7] the fact being confirmed by the effects of triethylamine added to the solvent system. Naphthylamines have also been shown to decrease their basicity, or in other words to increase the acidity, to a considerable amount in the excited state.[8] In the present case, the 313 nm light excites both the anilino chromophore (λ_{max}= ca. 297 nm in acetonitrile) and nitrophenoxy chromophore (λ_{max}= ca. 307 nm in acetonitrile). The excitation of the latter should lead to a dominant or at least detactable amount of the meta substitution product,[9] which is not the case. Hence, it may not be impertinent to assume that the excitation of the anilino moiety, followed by its acidity increase and proton transfer from the N-H group, is the main course of the photorearrangement.

It may be suspected the intramolecular exciplex formation of participating in the reaction. However the higher homologs of **1** (n=4 and 5) with least intramolecular interaction of charge-transfer[10a] and hydrogen bonding[10b] showed fairly large reactivity for the photoreaction. Therefore an exciplex formation or other intramolecular interactions could be regarded as minor factors in this reaction.

Summarizing the experimental facts so far obtained, the following reaction scheme may be proposed:



References and Notes

1) W. E. Truce, E. M. Kreider, and W. W. Brand, Org. React., 18, 99 (1970).

2) J. Cornelisse and E. Havinga, Chem. Rev., 75, 353 (1975); J. Cornelisse, G. P. de Gunst, and E. Havinga, Advan. Phys. Org. Chem., 11, 225 (1975).

3) K. Mutai and K. Kobayashi, unpublished work.

4) M. E. Kronenberg, A. van der Heyden, and E. Havinga, Rec. Trav. Chim. Pay-Bas, 86, 254 (1967).

5) H. E. Zimmerman and S. Somasekhara, J. Am. Chem. Soc., 85, 922 (1963).

6) J. J. C. Mulder. Quoted in E. Havinga, R. O. de Jongh, M. E. Kronenberg, Helv. Chim. Acta, 50, 2550 (1967), and E. Havinga and M. E. Kronenberg, Pure Appl. Chem., 16, 137 (1968).

7) Th. Förster, Z. Elektrochem., 54, 42 and 531 (1950); A. Weller, Discuss. Faraday Soc., 27, 28 (1959); N. Mataga and Y. Kaifu, Mol. Phys., 7, 137 (1964); H. Beens, K. H. Grellmann, M. Gurr, and A. H. Weller, Discuss. Faraday Soc., 39, 183 (1965).

8) Th. Förster, Z. Elektrochem., 54, 42 and 531 (1950); G. Jackson and G. Porter, Proc. Roy. Soc. (London), A260, 13 (1961).

9) Irradiation of m-$O_2NC_6H_4O(CH_2)_nNHPh$ (n=2 and 3) resulted in the substitution at the para position of the nitro group. Details will be reported in the near future.

10) a) K. Mutai, Tethedron Lett., 1971, 1125; b) M. Ōki and K. Mutai, Spectrochim. Acta, 25A, 1941 (1969).