January, 1982] © *1982 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.*, **55**, *317—318 (1982)*

Substituent Effect on a Photo-Smiles Rearrangement by Laser Photolysis

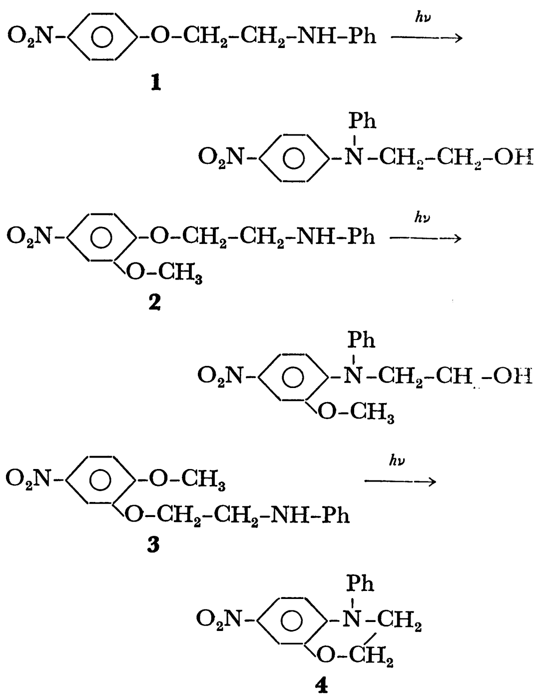
Kenji YOKOYAMA, Junko NAKAMURA, Kiyoshi MUTAI,† and Saburo NAGAKURA*
The Institute of Physical and Chemical Research, Wako, Saitama 351
† *Department of Chemistry, College of General Education, The University of Tokyo, Meguro-ku, Tokyo 153*

(Received July 4, 1981)

Synopsis. The photo-Smiles rearrangement was studied for two homologues of *N*-[2-(4-nitrophenoxy)ethyl]-aniline by laser photolysis, an importance being attached to the effect of the alkoxyl substituent on the reactive position. The nitro group enhances the substitution at the para position, but the alkoxyl group does not play a significant role in the photosubstitution of the molecules.

The photo-Smiles reaction of *N*-[2-(4-nitrophenoxy)-ethyl]aniline (**1**) is a typical example of intramolecular nucleophilic photosubstitution.1) In the previous study,1) the authors demonstrated by the aid of laser photolysis that this reaction proceeds *via* an intramolecular ion radical pair and the Meisenheimer-type complex. This means that the substitution takes place through interaction between the ground state cation and anion radicals in pair. From this point of view, it is reasonable that the photosubstitution reaction is para directing with regard to the NO_2 group as is usual for the thermal nucleophilic substitution. This is also supported by the theoretical consideration that in the nitrobenzene anion radical the free valency is larger at the para position than at the other positions, that is, the NO_2 group activates the para position.2)

Mutai *et al.*3) studied the photo-Smiles reaction of *N*-[2-(2-methoxy-4-nitrophenoxy)ethyl]aniline (**2**) and *N*-[2-(2-methoxy-5-nitrophenoxy)ethyl]aniline (**3**) in polar solvents by analyzing their final products and reported that the substitution takes place at the para position with regard to the NO_2 group.



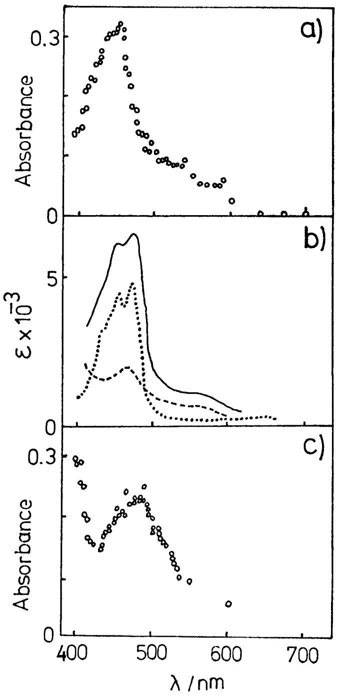


Fig. 1. a) Absorption spectrum of **a** 10 ns after the excitation. b) Broken line: absorption spectrum of the DMNB anion radical. Dotted line: absorption spectrum of the NMA cation radical. Solid line: the 1:1 superposition of the spectra of the DMNB anion and NMA cation radicals. c) $T_n \leftarrow T_1$ absorption spectrum of DMNB in the acetonitrile solution (present study).

These results indicate that NO_2 group plays a significant role in the photo-Smiles reactions. Therefore, in the present study, we have carried out the laser photolysis experiment of **2** and **3** together with **1** in acetonitrile to confirm the effect of NO_2 and CH_3O group upon the photosubstitution by elucidating their reaction mechanism directly.

1, **2**, and **3** were prepared as mentioned previously and purified by chromatography.3) 1,2-Dimethoxy-4-nitrobenzene (DMNB) (Aldrich Chemical Co.) was purified by a sublimation and repeating recrystallizations. Acetonitrile (Wako, spectroscopic grade) was used as solvent without further purifications. Sample solutions for transient absorption measurements were degassed by repeating freeze-and-thaw cycles. The transient absorption was measured with the same apparatus as mentioned previously.1,4)

Results and Discussion

The transient absorption of **2** was measured in the acetonitrile solution containing triethylamine (0.1 mol dm^{-3}) by the excitation with an N_2 laser at 337 nm.

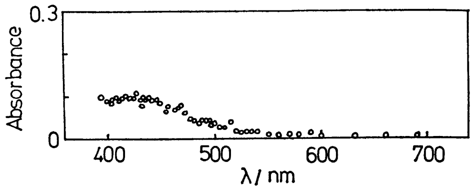


Fig. 2. Absorption spectrum of **b** 3 μs after the excitation.

It consists of two components, the faster one, **a**, and the slower one, **b**, their decay time constants being 35 ns and more than 200 μs, respectively. Figure 1a) shows the spectrum of **a**. Component **a** cannot be observed in nonpolar solvents like benzene and cyclohexane. Furthermore, the spectrum of **a** is different from $T_n \leftarrow T_1$ absorption spectrum of DMNB which is measured in the present study (see Fig. 1c)) and also from that of aniline and *N*,*N*-dimethylaniline.[5] In Fig. 1b) is shown a 1:1 superoposition of the spectrum of the DMNB anion radical[6] and that of the *N*-methylaniline (NMA) cation radical.[7] The superposition is very similar to the spectrum in Fig. 1a). Thus, **a** is assigned to an intramolecular ion radical pair, and the photosubstitution of **2** proceeds *via* the ion pair as that of **1** does.[1]

The other component, **b**, whose spectrum is shown in Fig. 2, is assigned to the relating Meisenheimer-type complex. The spectrum of **b** is not remarkably different from that of the relating complex of 1.[1] This implies that the conjugation of the CH_3O group with the residual system is not so significant for the complex. Polliff and Saunder showed that the spectra of 1,1-dimethoxy-2,6-dinitrocyclohexadienide and 1,1,4-trimethoxy-2,6-dinitrocyclohexadienide, are very similar to each other.[8]

These results mean that the photosubstitution reactions of **1** and **2** are very similar in their mechanism to each other. Particularly, the fact that the substitution takes place for **2** at the para position with regard to the NO_2 group shows that in the DMNB anion radical the NO_2 group activates the para position, but the CH_3O group does not play a significant role in activation of the benzene ring.

The acetonitrile solution of **3** shows the transient absorption with two components by the excitation with an N_2 laser. Both components of **3**, however, are different from those of **2**. The fast component of **3** rises up very fast and decays with the time constant of 1.0 μs, which is much larger than that of **2**, 35 ns. The slow component of **3** rises up with the time constant of 20 μs and does not decay within the time domain of the monitor light pulse (200 μs). Both components of **3** are not quenched by the addition of O_2 gas.

Figure 3a) and 3b) show the spectrum of the fast and slow components of **3**, respectively. The latter may be assigned to that of the final product, **4**, because both spectra are very similar to each other, as shown in Fig. 3b). The assignment of the fast component is not clear so far. The built up time constant of the slow one is twenty times larger than the decay time constant of the fast one. Consequently, the fast component is not a direct precursor of the slow component. These results suggest that the reaction mechanism of **3** is different from those of **1** and **2**, that is, the para directing character with regard to the NO_2 group in **3** should not be due to the same origin as in **1** and **2**.

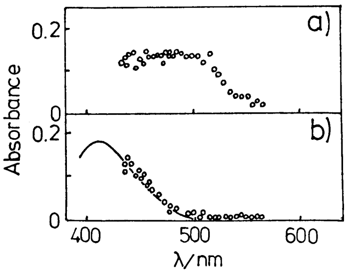


Fig. 3. Transient absorption spectrum of **3**.
a): Absorption spectrum of the fast component 10 ns after the excitation. b): Absorption spectrum of the slow component 45 μs after the excitation. Solid line; absorption spectrum of the final product, **4**.

The present study indicates that the orientation rule should be discussed taking not only the final products but also the respective reaction mechanisms into account. Furthermore, it is shown that in **1** and **2** the para directing character is due to the activation by the NO_2 group but not the CH_3O group. The reaction mechanism of **3** should be studied further.

References

1) K. Yokoyama, R. Nakagaki, J. Nakamura, K. Mutai, and S. Nagakura, *Bull. Chem. Soc. Jpn.*, **53**, 2472 (1980).

2) S. Nagakura and J. Tanaka, *Bull. Chem. Soc. Jpn.*, **32**, 734 (1959).

3) K. Mutai, S. Kanno, and K. Kobayashi, *Tetrahedron Lett.*, **1978**, 1273; K. Mutai and K. Kobayashi, *Bull. Chem. Soc. Jpn.*, **54**, 462 (1981); K. Mutai, K. Yokoyama, S. Kanno, and K. Kobayashi, *Bull. Chem. Soc. Jpn.*, to be submitted.

4) H. Hayashi and S. Nagakura, *Bull. Chem. Soc. Jpn.*, **53**, 1519 (1980).

5) K. D. Cadogan and A. C. Albrecht, *J. Phys. Chem.*, **73**, 1868 (1969).

6) T. Shida, private communication. The molecular absorption coefficient of the DMNB anion radical is estimated to be about 2000 at 455 nm.

7) T. Shida, Y. Nosaka, and T. Kato, *J. Phys. Chem.*, **82**, 695 (1978).

8) R. J. Polliff and B. C. Saunders, *J. Chem. Soc.*, **1964**, 1132.