

Bifunctional Reactivity of the Nitrophenoxyl Group in Intramolecular Photoreactions¹

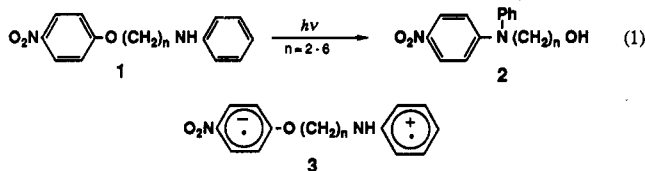
Kiyoshi Mutai,* Hideyuki Tukada, and Ryoichi Nakagaki†

Department of Chemistry, College of Arts and Sciences, The University of Tokyo, Komaba, Meguro-ku, Tokyo 153, Japan, and Faculty of Pharmaceutical Sciences, Kanazawa University, Takara-machi, Kanazawa 920, Japan

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The photochemical behavior of a homologous series of compounds, $p\text{-O}_2\text{NC}_6\text{H}_4\text{O}(\text{CH}_2)_n\text{NHPh}$ ($n = 2-10, 12$, and 16) in acetonitrile is reported. The lower ($n = 2-6$) homologues undergo an apparently nucleophilic type rearrangement to give ω -((*p*-nitrophenyl)amino)alkanol, while the higher homologues ($n \geq 8$) undergo an intramolecular photoredox reaction accompanied by C-N bond cleavage to give ω -((*p*-nitrosophenoxy)alkanal and aniline. The $n = 7$ homologue is situated at the switching point of these two reaction pathways, exhibiting neither type of photoreactions. Photoinduced intramolecular electron transfer to generate a radical ion pair is observed for all homologues, and the quantum yield decreases with increasing chain length. This species is the intermediate in the photorearrangement, for which the effect of base-catalysis is discussed in connection with the reaction mechanism. Comparison of the quantum yield for the electron transfer in 1 with that in 1-(anilinomethyl)-4-((*p*-nitrophenoxy)methyl)cyclohexane reveals the dominance of through-bond electron-transfer mechanism in the higher ($n \geq 6$) homologues. The reaction quantum yield vs chain length profile is discussed in terms of the relative quantum yield of the radical ion pair, the chain conformation, and the photoredox reaction mechanism.

In some bichromophoric chain molecules with an electron acceptor (A) and an electron donor (D) at the terminal ends, A-(CH₂)_n-D, photoirradiation in polar solvents induces a solvent-separated radical ion pair, which if the appropriate conditions are provided gives rise to a chemical process. A typical example is a homologous series of α -((*p*-nitrophenoxy)- ω -anilinoalkanes, $p\text{-O}_2\text{NC}_6\text{H}_4\text{O}(\text{CH}_2)_n\text{NHPh}$ 1(n), which undergoes rearrangement to yield 2² as a sole product of the recombination process of the corresponding radical ion pair (3)³ or a chemical species derived from it.⁴



The reactivity of each homologue decreases with chain length, and virtually no rearranged product is observed for 1(7), but further extension of the spacer chain length shows a new development of photoreaction. The present paper is concerned with the mechanism of the primary charge separation and the subsequent photoprocesses in this homologous series.

Results and Discussion

Photoreaction of the Higher Homologues ($n \geq 8$) of 1. Acetonitrile solutions of the $n \geq 8$ homologues were irradiated with a 500-W Xe arc filtered through colored-glass filters, or, in a preparative scale, with a 100-W high-pressure Hg lamp immersed in the solution through a Pyrex filter. The reaction was monitored by using a UV-vis spectrophotometer and high-performance liquid chromatography (HPLC). As illustrated in Figure 1a for 1(12) (in this section, this homologue is adopted as an example representing typical behavior of the higher homologues) the absorption curves show a decrease at ca. 310 nm and an increase at ca. 340 nm with increasing irradiation time, suggesting disappearance of the *p*-nitrophenoxyl chromophore and appearance of a new product(s). Because the absorption maximum of 2 is at ca. 395 nm, it is clear that the *p*-nitrophenoxyl group in the starting

material underwent a different conversion from that in eq 1. An HPLC analysis revealed two new components as major products. However, several attempts to isolate them were unsuccessful; evaporation of the solvent under reduced pressure from the irradiated solution resulted in production of a tarry brown substance that was insoluble in most organic solvents. This phenomenon is possibly a result of the reaction between the solute molecules in the concentrated solution, because the irradiated solution kept in the dark at ambient temperature under air for a few days showed no change in the high-performance liquid chromatogram or no sign of precipitation.

We adopted LC-UV method for the characterization of the photoproducts; UV-absorption curves of each component were obtained by plotting the peak area in a chromatogram recorded under a constant condition as a function of wavelength (Figure 1b). One of the two components other than the starting material was identified as aniline by comparison of the LC-UV spectrum and retention time with those of the authentic sample. The spectral curve of the other component with maxima at 240 and 345 nm is very similar to that of *p*-nitrosoanisole. In order to determine the structure of this product, 400-MHz ¹H NMR spectrum of the irradiated solution in acetonitrile (8×10^{-4} M) was measured. New signals at δ 9.70 (t) and 2.41 (m) can respectively be assigned to the formyl group and the adjacent methylene group, CH₂CHO, and new signals in the aromatic proton region (7.13 and 7.94, both doublets) and a new triplet (4.17) adjacent to the one due to the original CH₂O group suggest a large structural change in the nitro group. Additionally, broadness of the doublet at 7.94 is a characteristic feature of the presence of nitroso group as a substituent, underlining the conclusion obtained from LC-UV spectrum. Because the photoreaction was conducted in a highly diluted solution (10^{-4} M or less) and there was no evidence for the participation of the solvent molecule as a reactant, the structure of the remaining major product was assigned to a nitrosoaldehyde 4. Thus the reaction should be interpreted as an intra-

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* Kanazawa University.

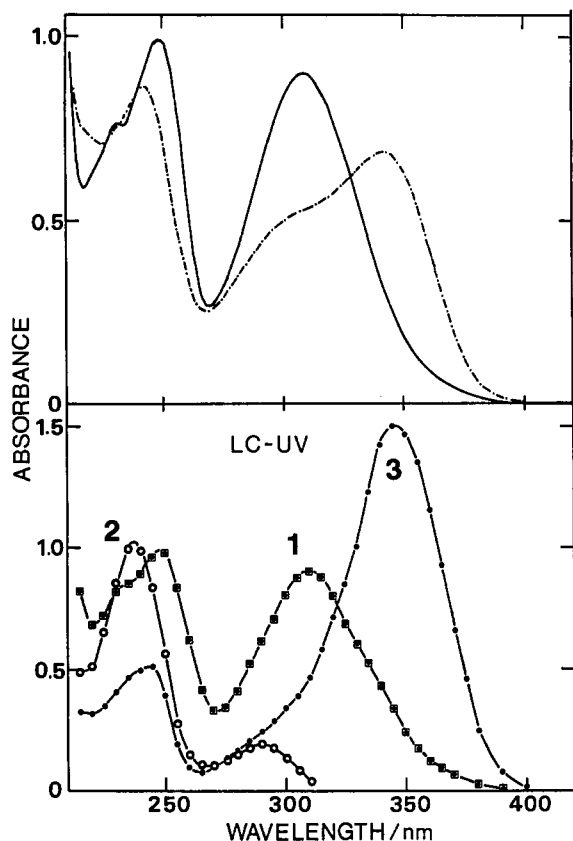
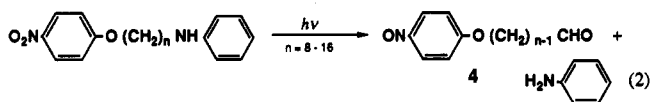


Figure 1. Top: Absorption spectra of 1(12) (—, before irradiation; ---, after 16 min of irradiation) in acetonitrile. Bottom: LC-UV spectra of irradiated solution of 1(12), obtained by plotting each peak area in high-performance liquid chromatogram against wavelength (1, 1; 2, aniline; 3, product 4).

molecular redox type (eq 2), involving the transfer of an oxygen atom of the nitro group to the methylene carbon next to the anilino group with concomitant cleavage of the C-N bond.

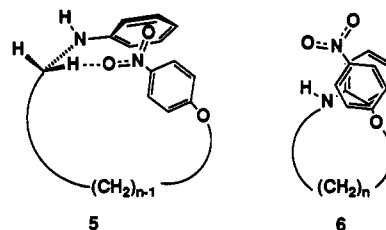


Various types of photoreduction of the nitro group are well documented,⁵ but the dependence of the reaction pathway on chain length in a homologous series has no precedent, so far as we know. This fact has prompted us to make a further search of the reactions for the following problems: (1) elucidation of the factors controlling the bifunctional reactivity of *p*-nitrophenoxyl group, (2) detection of an intermediate that dominates the course of the photoredox reaction, and (3) study of the effects of the chain length on the reactivity and pathway.

Comparison between the Intramolecular and Intermolecular Reactions. On steady-state irradiation of an acetonitrile solution of *N*-methylaniline and *p*-nitroanisole (7×10^{-5} M in each), a small but definite amount of aniline and *p*-nitrosoanisole were identified as reaction products. Similar intermolecular type of photooxidative dealkylations of *N*-alkylanilines by a nitro oxygen have also been reported.⁶ No nucleophilic substitution product

(such as *N*-methyl-*p*-nitrodiphenylamine) was detected in the reaction mixture by means of HPLC and UV absorption spectroscopy. The long-chain homologues can therefore be regarded as an intramolecular structure modification of the corresponding intermolecular photo-reactive system.

A most probable reason for the absence of the photoredox reaction in the lower homologues is as follows: an essential process common to the mechanisms so far proposed for photoredox reactions of nitro aromatic compounds⁵ is initial abstraction of a hydrogen atom from an active methylene group by an oxygen atom of the nitro group. This process requires a cyclic transient conformation realized only when the relative disposition of the two terminal aromatic rings is in an approximately head-to-tail geometry (5). This conformation, however, is virtually impossible in the lower homologues, because of the limit of the short polymethylene chains. For these lower homologues, the only available conformation with the two aromatic rings in close proximity is a head-to-head type 6, which leads to no other than the rearrangement to yield 2. It is noteworthy that the intramolecular photosubsti-



tution (or photorearrangement) observed in the lower homologues (eq 1) has no corresponding intermolecular counterpart.⁸ Furthermore, in the higher homologues, access of the anilino nitrogen to the aromatic carbon atom attached to the ether oxygen is not conformationally restricted, but the corresponding photosubstitution product was not observed. The results so far accumulated from the photochemical behavior of the homologues of 1 and from the above intermolecular model suggest that the *p*-nitrophenoxyl group has two sites for photoreaction: one is the oxygen atom of the nitro group and the other the ring carbon atom attached to the ether oxygen. Under the circumstances where these two sites are freely available for the reactions, the photoredox reaction is much more dominant than the photosubstitution. The photorearrangement was therefore a second choice for the excited *p*-nitrophenoxyl group. In other words, the intramolecular photosubstitution observed in the lower homologues of 1 ($n = 2-6$) may be regarded as a "forced" reaction. So far as we know, this is one of the rare cases in which the chain-length-dependent complete switching of the pathway is observed in photochemical reaction.¹⁰

The above interpretation for the chain length effect on

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the reaction course is substantiated by the fact that the intramolecular photodimerization, requiring a face-to-face conformation for the formation of an exciplex, of α,ω -di-maleimidoalkanes has been observed only for the derivatives of octane (eight spacer atoms, corresponding to 1(6)) and the lower alkanes,¹¹ which in regard to the number of the methylenes or spacer atoms is in good accord with the homologues of 1, supposed to undergo the photorearrangement through the conformation 6. On the other hand, the fact that the photoredox reaction was observed for $n = 8$ and the higher homologues indicates that the eighth methylene group counting from the nitrophenoxyl side is the first falling within the reaction range of the nitro group in the conformation 5. Breslow¹² and Winnik¹³ have reported that intramolecular hydrogen abstraction by an excited ketone carbonyl group from the polymethylene chain of the ester alkyl group in p -(PhCO) C_6H_4 COO-(CH₂) $_n$ CH₃ occurs at the carbon atoms of $n \geq 9$ irrespective of the total chain length. Similar results have been reported by Tanimoto et al. for the intramolecular hydrogen abstraction by the photoexcited anthraquinone group in alkyl 2-anthraquinonecarboxylate.¹⁴ Since the van der Waals radii of the N-O moiety in the nitro group (0.155 nm) and carbonyl group (0.150 nm)¹⁵ are nearly the same, if we assume that the reaction range of these groups are approximately the same and that the coplanarity of the carboxylate group with the aromatic ring imposes greater restrictions on the mobility of the polymethylene chain than the ether oxygen in 1, the results obtained from the benzophenone derivatives are in good agreement with the present case and hence the observed switching to the much more favorable redox reaction is mostly due to the availability of a methylene group within a reaction range of the nitro group.

Photoinduced Generation of 3. It has been reported by Yokoyama et al. that 1(2) undergoes two-photon reduction when irradiated with a high-density (focused) laser beam, yielding nitrosophenoxyl chromophore,¹⁶ though they did not either isolate or chemically identify the product. They suggested that the process leading to the nitroso group is simple cleavage of the N-O bond in the locally excited nitro group. On the other hand, the photoredox reaction of 1(12) was found to be a one-photon process on the basis of the linear relationship obtained by plotting the product yield against the intensity of an incident light from a Xenon arc. A one-photon mode has also been found in the photorearrangement of 1(2) irradiated with a defocused laser beam, consistent with the intermediacy of the radical ion pair 3 generated by photoinduced intramolecular electron transfer.

Electron transfer is now generally accepted as the primary process in the photoredox reactions of the nitro aromatics with aromatic or aliphatic amines to generate the corresponding radical anions of nitro compounds,^{5c,d,6,9,17} hence 3 is a possible candidate for the intermediate in this intramolecular photoredox reaction. In

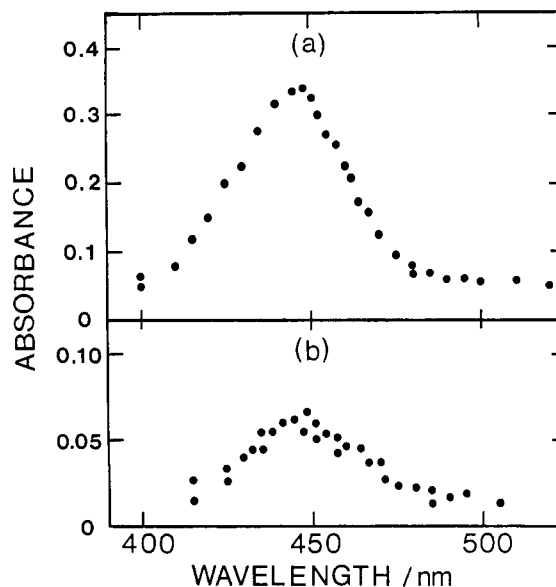


Figure 2. Transient absorption spectra of (a) 1(2) and (b) 1(12) in acetonitrile, recorded 20 ns after triggering. Excitation wavelength = 308 nm (XeCl excimer laser). The concentration of the solutions was 7×10^{-5} mol/L.

Table I. Quantum Yields of the Photoreactions of 1 and Relative Quantum Yields of Radical Ion Pair

n	quantum yields of the photoreactions	relative quantum yields, Φ_{\pm}
2	4×10^{-5}	0.233 ± 0.015
3	8×10^{-5}	0.210 ± 0.015
4	1.2×10^{-2}	0.176 ± 0.015
5	4.2×10^{-3}	0.129 ± 0.015
6	1.5×10^{-4}	0.048 ± 0.01
7	2.2×10^{-4}	0.025 ± 0.01
8	4.2×10^{-4}	0.022 ± 0.01
9	1.4×10^{-3}	0.015 ± 0.01
10	2.5×10^{-3}	0.014 ± 0.01
12	2.9×10^{-3}	0.016 ± 0.01
16	2.8×10^{-3}	0.012 ± 0.01
compound 7		0.102 ± 0.01

order to test this possibility, laser flash study of 1(12) was carried out. The transient absorption spectrum observed by irradiation of p -nitrophenoxyl group of 1(12) with 308-nm light was illustrated in Figure 2 with that of 1(2). The spectrum of 1(2) (Figure 2a) has been assigned to that of the solvent-separated radical ion pair 3 on the basis of close similarity to the superposed absorption spectra of the corresponding donor cation and acceptor anion.³ Because the transient absorption spectrum of 1(12) (Figure 2b) is very much similar to that of 1(2), the observed photoprocess of this homologue is also characterized as charge separation in the excited state, i.e. formation of a solvent-separated radical ion pair in acetonitrile, though the amount of 3(12) generated was much smaller than that of 3(2).

This supposedly long-range phenomenon interested us to study the effect of the chain length. The decay curves of the transient absorption monitored at 450 nm, appearing 40–50 ns after excitation with 308-nm laser pulse were shown for the $n = 2, 4, 6, 8, 10,$ and 12 homologues in Figure 3. In all homologues a sharp peak and slow decay pattern were observed. Each pattern is an average of three (six for 1(8) and 1(10)) successive flash photolyses, and the data summarized in Table I are the average of three or more sets of the observations thus obtained.

In Figure 4, the relationship of the relative quantum yields Φ_{\pm} with the chain length is illustrated. The observed

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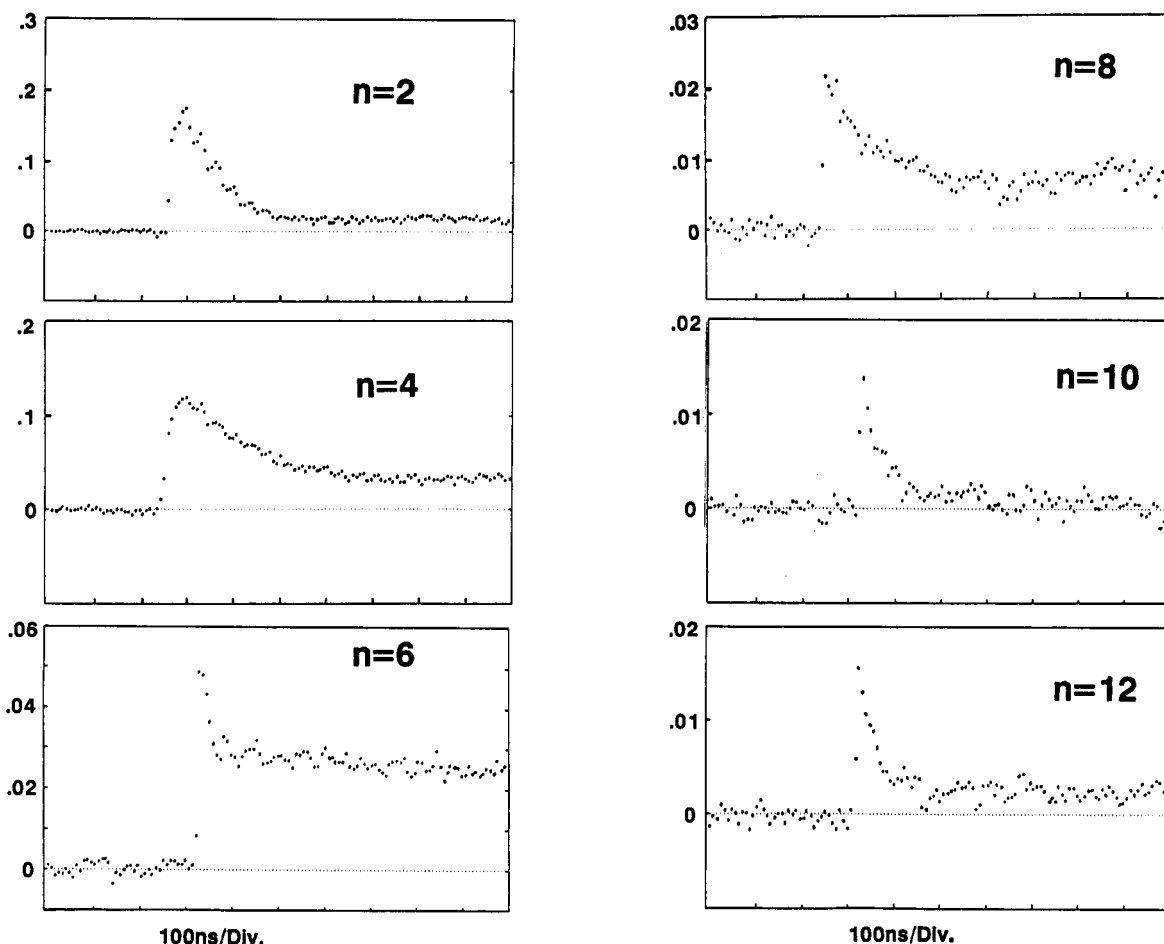


Figure 3. Decay curves of transient absorption at 450 nm of 1 ($n = 2, 4, 6, 8, 10,$ and 12) in acetonitrile: ordinate, relative intensity; abscissa, time (100 ns/division).

peak intensity can be regarded as directly proportional to the quantum yield of the production of the radical ion pair, because all the homologues show almost the same molar extinction coefficient at the absorption peak of 308 nm, characteristic of *p*-nitrophenoxyl moiety, and the concentration of the solutions was so adjusted that the solutions had almost the same absorbance (within a range of $\pm 1.5\%$) at this wavelength. The magnitude of the error bars in Figure 4 is dependent partly on the relative intensity of signal vs electric noise and mainly on the fluctuation of the intensity of the incident laser flash. Hence increase of the number of observations did not necessarily lead to the convergence of the average value. For the higher homologues with a low yield of 3, the length of the error bar is so drawn as to include as many observed points as possible. Consequently it should be noted that the line drawn through the circles is merely a tentative one, especially in the region from $n = 7$ –16. As expected, the quantum yields for the higher homologues are low, but it is noticeable that the generation of 3 is observed even in 1(16).

Mechanisms of the Photoelectron Transfer. The generation of 3 in the higher homologs with the A-D pair separated with a long chain is surprising, especially if we assume through-space mechanism for the electron transfer, in which close proximity of the A and D aromatic rings is required. For the lower homologues, 1(2) and 1(3), this mechanism has been suspected, because the fluorescence from intramolecular exciplex of 1 has been observed in nonpolar solvents but not in polar solvents,¹⁸ i.e. an ex-

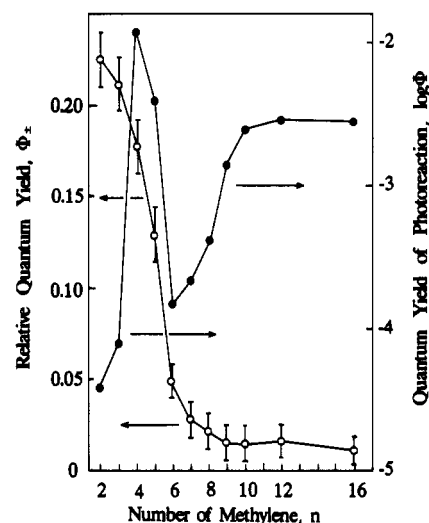


Figure 4. Plots of relative quantum yields for 3 (open circles) and of quantum yields of the photoreactions of 1 (filled circles) against the number of methylene groups in polymethylene chain.

ciplex formed in such a polar solvent as acetonitrile generally separates into a nonfluorescent solvated ion pair.^{19,20} This possibility is underlined from the similar photophysical behavior of the closely related analogues, *p*-

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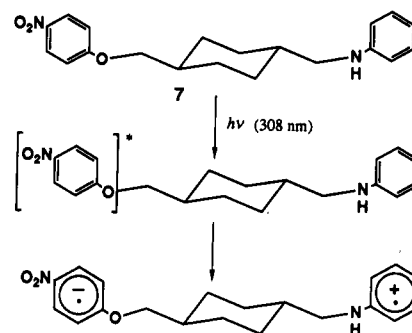
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$O_2NC_6H_4(CH_2)_nNHP$.²¹ On one hand, the fact that the excimer fluorescence is observed in $Pyr(CH_2)_nPyr$ ($Pyr = 1$ -pyrenyl) for the higher homologues ($n = 9$ –22) as well as for the lower homologues ($n = 2$ –6)²² can be cited as supporting evidence for the through-space process. On the other hand, the mechanism, if possible, is perhaps of minor contribution, especially in nitroaromatic compounds, to the formation of **3**, because the fluorescence is accompanied with the decay of the singlet exciplex formed from the *p*-nitrophenoxyl chromophore in the singlet excited state, but this state competitively undergoes rapid degradation to the triplet state.

As an alternative mechanism of photoinduced electron transfer, through-bond process involving σ - π interaction has recently been proposed in the study of structurally rigid systems,^{23–25} characterized as a long-range, fast, and highly efficient effect. This mechanism has also been suspected in the generation of **3** from partly immobilized **1(2)** as an inclusion complex with α -cyclodextrin dissolved in aqueous DMSO.²⁶ From the results obtained for several rigid systems, a zigzag or all-trans conformation of a σ -C-C system has been suggested to be more favorable for through-bond electron transfer than the system displaced with one or more gauche conformations.²⁵ Thus for a flexible system such as **1**, the contribution of each chain conformation to the electron transfer is difficult to estimate, and no definite conclusion on the mechanism can be drawn merely from the curve of the relative quantum yield in Figure 4.

In order to elucidate this problem, we used a rigid model of cyclohexane derivative, *trans*-1-(anilinomethyl)-4-(*p*-nitrophenoxymethyl)cyclohexane (**7**) with the corresponding DCH_2 and ACH_2 groups at the 1- and 4-positions

in the *trans* configuration, which does not allow π - π overlap between A and D moieties in either 1,4-diaxial or 1,4-diequatorial conformation. Upon irradiation with a laser



flash of an acetonitrile solution of **7** under the same conditions as employed for **1**, a transient spectrum similar to that of **3** with an intensity comparable to the transient peak of **1(5)** was observed. Thus the through-bond electron-transfer mechanism was unambiguously proved to take place in **7**. In the number of the spacer atom intervening the A-D pair, the model compound corresponds to **1(6)**, but the quantum yield for **7** exceeds **1(6)** by a factor of 2.2. The difference may be attributed to the flexibility of the spacers between the two; the rigid structure with C_1 -(t)- C_2 -(g)- C_3 -(t)- C_4 conformation is more favorable than the polymethylene with more gauche conformation in average. Hence it is reasonable to conclude that in **1(6)** and probably in the higher homologues ($n \geq 7$) the charge separation occurs predominantly by the through-bond mechanism. For **1(5)**, an almost equivalent intensity to **7** suggests the dominance of the through-bond mechanism in this homologue.

Reactivity and Chain Length.²⁷ The above results of the quantum yield for **3** and the number of the methylene group *n* profile prompted us to study the relationship between the quantum yield of the photoreaction and *n*, especially because the through-bond mechanism for the formation of **3** makes it an unnecessary requirement for the A-D pair to be in close proximity at the time of excitation or during the lifetime of the excited state. It seems thus imperative to reexamine the mechanism of the rearrangement proposed on the basis of the through-space formation of **3**.²⁸

The quantum yield of the photorearrangement of **1(4)** upon irradiation at 313 nm in acetonitrile was determined to be 0.012. For the other homologues that exhibited too low yields to be determined directly, the values were estimated from the relative rate constants. The data are summarized in Table I and also depicted in Figure 4. The comparison of the reactivity of photorearrangement and photoredox reaction on a common scale is possible, because both the reactions are initiated by the excitation of *p*-nitrophenoxyl chromophore and the intramolecular reactions are essentially unimolecular. The reactivity vs chain-length profile in Figure 4 shows some characteristic features common to cyclization reactions such as lactone formation from ω -bromo carboxylate,²⁹ or ketone formation from α,ω -dicyanoalkanes;³⁰ that is, the curve reaches a maximum at the small number of *n*, passes through a

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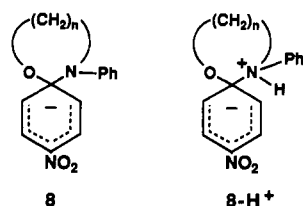
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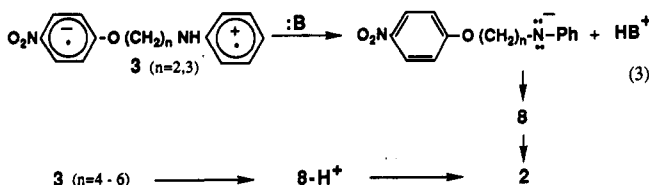
minimum at the medium, and levels off at the large number. Similar features of the chain-length effects on chemical process,³¹⁻³³ though some of them³⁴ are less systematically studied, have also been reported, suggesting that the chain extension does not necessarily incur the constant reduction of the reactivity.

The extremely small values observed for 1(2) and 1(3) in the order of 10^{-5} may be regarded as suggesting no reaction, but prolonged irradiation clearly exhibited an increase of the absorbance at 395 nm corresponding to the peak of the rearranged product 2. A quantum yield of 6×10^{-4} for 1(2) has been reported by Wubbels et al. from the kinetic analysis.⁴ The difference, probably due to the different procedures adopted for the determination, should be admitted for this small value.

Although intramolecular reactions of bifunctional molecules more or less undergo conformational restrictions, the encounter probability of the reacting moieties attached to a flexible spacer is far greater than that in the corresponding intermolecular reactions. In other words, from the view point of activation entropy, intramolecular reactions are expected to be more favorable than the corresponding intermolecular reactions. In this regard, the quantum yields for the reaction of the lowest two homologues are unexpectedly low; for the lower homologues of $n = 2-6$, the reactivity order of $n = 2 > 3 > 4 > 5 > 6$ was predicted, because the relative quantum yield of the intermediate 3 is in this order and a spiro Meisenheimer complex 8 or 8-H⁺ in the subsequent step is far more easily



formed with a five- ($n = 2$) or a six-membered ($n = 3$) ring than that with a larger ring. The observed low reactivity of 1(2) and 1(3) should be attributed to the absence of base catalysts as has been found by us² and kinetically analyzed in detail by Wubbels;⁴ the anilino radical cation in 3 transfers an NH proton to the base to form an anilide anion, as a result of ensuing electron transfer from the radical anion to the anilino radical (eq 3), which in turn



attacks at the ring carbon atom of the *p*-nitrophenoxyl

moiety. In the absence of the catalyst, the excitation induces charge separation more effectively than in the higher homologues but probably a fast electron-return process (either by through-bond or through-space mechanism) reduces the molecule to the ground state, resulting in the very low quantum yields.

The effect of the base catalysts on the reactivity is interesting but perplexing; for instance, triethylamine used as a typical base catalyst in the photorearrangement is effective only for the $n = 2$ and 3 homologues, but not for the rearrangement of the higher homologues of $n = 4-6$, in which the amine reduces the rate of the production of 2.² This latter phenomenon is probably caused by competitive reaction of the amine with the nitro group of 1 or 2, because in the presence of the amine the UV spectra of these homologues showed remarkably different features, exhibiting a new peak at ca. 280 nm in addition to the spectrum of 2. This type photoreaction has often been observed in a solution of an aliphatic amine and a nitroaromatic compound.³⁵

It may be argued that the amine not only reacts with the nitro group but also catalyzes the photorearrangement in the higher homologues but the lower efficiencies of the generation of the radical ion pair and of its recombination to yield 8 result in the apparent acceleration of the intermolecular reaction and suppression of the rearrangement. Longer lifetime of 3(4) (253 ns) than 3(2) (87 ns) obtained from Figure 4 may be cited as evidence for the lower efficiency of the recombination of 1(4). In order to scrutinize this possibility, we adopted pyridine as a catalyst, since this base has no NCH₂ group susceptible to an excited nitro aromatic compound. Irradiation of the acetonitrile solutions of 1(4) containing pyridine in a range of 0.99×10^{-4} through 5.9×10^{-2} mol/L was carried out under the similar conditions applied to those containing triethylamine. The quantum yield observed was independent of the concentration of pyridine, i.e. identical with the value obtained in the absence of the base. This finding suggests that the pathways following the generation of 3 to the rearranged product 2 are different between 1($n = 2$ and 3) and 1($n = 4-6$) (eq 3). For the latter homologues, a mechanism best fit for these findings is direct radical recombination of 3²⁸ to generate 8-H⁺, which through intramolecular hydrogen shift and O-Ar bond cleavage yields the rearranged product 2 without the participation of a base catalyst.

In connection with this, it may be worth mentioning that thermal rearrangement of 1($n = 2$) to give 2 in DMF was observed almost at an instant of the addition of NaOMe at ambient temperature and, on the contrary, 1(4) and the higher homologues showed no detectable change under the same conditions or at higher temperature (100 °C) even after a few days.³⁶ The results suggest that the lowest two homologues are extremely reactive once the anilide type anionic species, if formed either photochemically or thermally, cannot be an effective intermediate for the rearrangement.

The smooth decrease of the quantum yield from 1(4) through 1(6) is probably a reflection of the difficulty of forming medium-sized spiro rings in 8-H⁺ (a sharp decrease of the quantum yield by a factor of 28 from 1(5) to 1(6), which corresponds to from eight- to nine-membered spiro

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ring, is a typical example). It is worth noting that the eight- and nine-membered spiro-type complexes 8-H^+ can still be formed in the photoreaction, but not in the base-catalyzed thermal reaction.

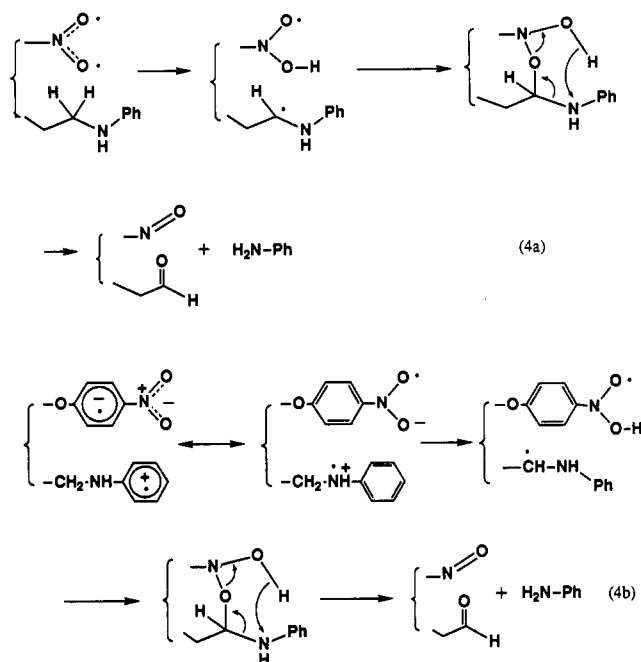
It should be noted that 1(7) with a higher quantum yield of disappearance than 1(2) gave no rearranged product, the difference suggesting the presence of an effective quenching process in 1(2). The point of 1(7) in Figure 4 is specific because the quantum yield was low and only a trace of aniline was detected by HPLC in the reaction mixture even after several hours of irradiation. Although the production of aniline may suggest the photoredox reaction, no trace of its counterpart product 4, 7-(*p*-nitrosophenoxy)heptanal, was found in an irradiated solution spectroscopically. Thus, aniline was probably a product of quite a different mechanism other than those working in the photorearrangement and photoredox reaction, for instance, intermolecular photoredox reaction. The reason for this low reactivity is partly due to the difficulty to form a 10-membered spiro-Meisenheimer complex in the pathway of the photorearrangement and partly due to unavailability of the methylene group adjacent to the anilino group in the photoredox reaction, in addition to the very low yield of the radical ion pair.

The major cause of the reactivity increase in the higher homologues is probably a reflection of the increase of the probability of the reacting methylene group falling in the reaction range of the nitro group and also, as molecular models show, of the reduction of the conformational restraint on the activation energy of the hydrogen abstraction. This latter factor is probably reflected in the order of the reaction quantum yields, $1(8) < 1(9) < 1(10)$.

The probability of the access of the two terminal groups in polymethylene compounds has also been a subject of theoretical consideration, in connection with the conformation of polymers,^{13c,37,38} and the conclusion is that a moderate chance of access of the terminal groups is expected for long-chain homologues, underlining the generality of the characteristic features described above.

There are two possibilities for the mechanism of this reaction (eq 4); one is through an excited nitroaromatic moiety, which abstracts hydrogen to form a cyclic transient species (4a), and the other through 3, which after proton transfer generates the same cyclic species (4b). Both mechanisms are so constructed as to involve a radical pair, because magnetic field effects on the rate of this photoreaction revealed that the reaction proceeds through an intersystem crossing process of a radical pair as one of the rate-determining steps.^{39,40} In order to satisfy this requirement, in mechanism 4b a proton is transferred from the CH_2 group to the nitro oxygen, but this process is least probable, because the radical cation has a much more acidic proton on the nitrogen adjacent to this methylene group, as is noted in the mechanism of the photorearrangement (eq 3). The mechanism 4a is therefore more probable than 4b.

The details of the mechanisms will be published in the near future.



Experimental Section

General. ^1H NMR spectra were recorded on Varian EM-390 (90 MHz) or JEOL-GX400 spectrometers. Melting points are uncorrected. Homogeneity of the starting materials and components of the reaction mixture were established by HPLC on a JASCO 880-PU with a reverse-phase column packed with Fine SIL C₁₈-5 using methanol as an eluent.

Materials. The procedures of the preparation and properties of the lower homologues of 1 ($n = 2-6$) have already been reported. Preparation of the higher homologues has been done as follows (the mp's, yields, and results of elemental analyses are summarized in Table II).

(i) **Preparation of ω -(*p*-Nitrophenoxy)alkyl Bromide.** A mixture of 1.39 g (10 mmol) of *p*-nitrophenol, 12 mmol of α,ω -dibromoalkane, 1.0 g (9.2 mmol) of potassium carbonate, and 0.3 g (1 mmol) of tetrabutylammonium bromide in 20 mL of water was heated at 110 °C for 3 h with stirring. After cooling, the reaction mixture was extracted with three portions of 10-mL chloroform. The combined extracts were dried over anhydrous potassium carbonate and filtered. The solvent was removed in vacuo, and the residue was separated by column chromatography, using silica gel (Wakogel C-200, Wako Chemicals).

All the homologues listed in Table II show similar ^1H NMR spectra (90 MHz, CDCl_3): δ 1.1-1.2 (2($n-2$) H, m), 3.40 ± 0.03 (2 H, t, $J = 6$), 4.02 ± 0.02 (2 H, t, $J = 7$), 6.91 ± 0.03 (2 H, d, $J = 9$), 8.16 ± 0.03 (2 H, d, $J = 9$).

(ii) **Preparation of 1.** A mixture of ω -(*p*-nitrophenoxy)alkyl bromide (2 mmol) and aniline (1 mL) was heated at 95-100 °C for 1.5 h. After cooling, the solid mass was triturated with 10 mL of 10% aqueous sodium carbonate and 10 mL of chloroform. The organic layer was separated, and the aqueous layer was extracted with two 10-mL portions of chloroform. The combined extracts were dried over magnesium sulfate and filtered. The solvent and unreacted aniline were removed in vacuo, and the remaining residue was charged on a silica gel column and eluted with a *n*-hexane-dichloromethane (1:1) mixture. The product (yellow crystalline) was purified by recrystallization from ethanol.

All the homologues show similar ^1H NMR spectra (90 MHz, CDCl_3): δ 1.0-2.0 (2($n-1$) H, m), 3.09 ± 0.01 (2 H, t, $J = 6$), ca. 3.5 (1 H, br s), 4.02 ± 0.01 (2 H, t, $J = 7$), $6.4-7.2$ (5 H, m), 6.90 ± 0.02 (2 H, d, $J = 9$), 8.17 ± 0.02 (2 H, $J = 9$). UV spectra in CH_3CN : $n = 2$, $\lambda_{\text{max}} = 304.5$ nm (ϵ 13 600); $n = 3$, 306.5 nm (13 800); $n = 4$, 307 nm (13 900); $n = 5$ and 6, 307 nm (13 600); $n \geq 7$, 307.5 nm (13 200 \pm 100).

(iii) ***trans*-1-(*p*-Nitrophenoxy)methyl)-4-(bromomethyl)cyclohexane.** A mixture of 1.35 g (5 mmol) of *trans*-1,4-bis(bromomethyl)cyclohexane, 0.70 g (5 mmol) of *p*-nitrophenol, and 0.40 g (2.9 mmol) of potassium carbonate in 5 mL

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Table II. Melting Points, Yields, and Results of Elemental Analyses of p -O₂NC₆H₄O(CH₂)_nX

n	molecular formula	mp, °C	yield, %	calcd			found		
				C	H	N	C	H	N
X = Br									
7	C ₁₃ H ₁₈ NO ₃ Br	51.5–52.5	49	49.38	5.74	4.43	49.18	5.68	4.47
8	C ₁₄ H ₂₀ NO ₃ Br	46.5–47.5	43	51.09	5.98	4.42	50.92	6.10	4.24
9	C ₁₅ H ₂₂ NO ₃ Br	50–51	49	52.33	6.44	4.07	52.22	6.54	4.07
10	C ₁₆ H ₂₄ NO ₃ Br	58–59	52	53.64	6.75	3.91	53.43	6.94	3.83
12	C ₁₈ H ₂₈ NO ₃ Br	51–52	53	55.96	7.30	3.63	55.93	7.49	3.64
16	C ₂₂ H ₃₈ NO ₃ Br	65.5–66.5	57	59.72	8.20	3.17	59.93	8.01	3.10
X = NHPH (1)									
7	C ₁₉ H ₂₄ N ₂ O ₃	66–67 (72–73) ^a	89	69.49	7.37	8.53	69.39	7.40	8.59
8	C ₂₀ H ₂₆ N ₂ O ₃	99–100	85	70.15	7.65	8.18	69.92	7.51	8.05
9	C ₂₁ H ₂₈ N ₂ O ₃	69–70	94	70.76	7.92	7.86	70.59	7.75	7.98
10	C ₂₂ H ₃₀ N ₂ O ₃	79–80	90	71.32	8.16	7.56	71.29	8.07	7.60
12	C ₂₄ H ₃₄ N ₂ O ₃	80–81	98	72.33	8.60	7.03	72.59	8.55	6.85
16	C ₂₈ H ₄₂ N ₂ O ₃	82–83.5	96	73.97	9.31	6.16	73.67	9.30	5.92

^a Polymorphism.

of DMF was heated at 90 °C with stirring for 2 h. After cooling, the reaction mixture was poured in 30 mL of water and extracted with three portions of 10 mL of dichloromethane. The combined extracts were dried over anhydrous potassium carbonate and filtered. The solvent was removed in vacuo, and the residue was separated by column chromatography, using silica gel (Wakogel C-200). Colorless crystals (0.75 g, 46%), mp 78–79 °C. ¹H NMR (90 MHz, CDCl₃): δ 0.9–2.2 (10 H, m), 3.31 (2 H, d, *J* = 6), 3.85 (2 H, d, *J* = 5), 6.93 (2 H, d, *J* = 9), 8.20 (2 H, d, *J* = 9). Anal. Calcd for C₁₄H₁₈NO₃Br: C, 51.23; H, 5.53; N, 4.27. Found: C, 51.33; H, 5.54; N, 4.33.

(v) *trans*-1-(Anilinoethyl)-4-(*p*-nitrophenoxymethyl)cyclohexane (7). This compound was prepared in a similar procedure as adopted for the synthesis of 1 from the corresponding bromide and aniline. Yield 87%. Pale yellow crystals, mp 131–132 °C. ¹H NMR (90 MHz, CDCl₃): δ 0.9–2.1 (10 H, m), 3.01 (2 H, d, *J* = 6), 3.85 (2 H, d, *J* = 6), 6.5–7.3 (5 H, m), 6.93 (2 H, d, *J* = 9), 8.17 (2 H, d, *J* = 9). Anal. Calcd for C₂₀H₂₄N₂O₃: C, 70.57; H, 7.11; N, 8.23. Found: C, 70.37; H, 7.00; N, 8.08.

Photochemistry. Sample solutions were deaerated by several freeze–pump–thaw cycles and sealed off under vacuum before irradiation.

(i) **Spectrophotometry.** LC–UV spectra were recorded with the aid of a Waters Model 481 LC spectrophotometer attached to a Waters Model 590 high-performance liquid chromatograph. Degassed solutions in 1-cm quartz cells were mostly irradiated with UV light from a Ushio 500W Xenon arc filtered by a combination of Toshiba glass filters (UV-D33S, UV-33, and UV-25), which mainly excites the acceptor moiety.

(ii) **Laser Photolysis.** An excimer laser, Lambda Physik EMG 50E, was used as an excitation light source. The exciting light pulse at 308 nm had width of ca. 10 ns (FWHM). A xenon flash lamp (EG&G FX-200) was employed as a detecting light source.

The laser photolysis apparatus consists of the excimer laser, the Xe flash, a Jobin-Yvon HR-320 monochromator, a Hamamatsu R-928 photomultiplier, and an Iwatsu TS-8123 digital oscilloscope. The output signal from the oscilloscope was transferred to a personal computer NEC-9801VM. In order to avoid multiphoton processes, the excitation laser beam was not focused onto quartz cells containing deaerated sample solutions.

(iii) **Quantum Yield of Photoreactions.** Because the reactivity of the most of the homologues was very low, the quantum yield for 1(4) was directly determined, and the yields for the other homologues were estimated from their relative reaction rate constants in comparison with that of 1(4).

The rate constants for the higher homologues (*n* ≥ 6) in steady-state photolysis were determined according to a procedure similar to that applied to the lower homologues (*n* = 2–6).² Namely, sample solutions containing the equal molar amount of the parent compounds were photolyzed under the same irradiation conditions, and the disappearance of the starting species and the increase of the nitrosoaldehyde 4 were monitored by HPLC.

The quantum yield for 1(4) was determined by using a 150W Xe arc as a light source, a Bausch & Lomb monochromator, and IL 700A (International Light) as a photon counter. Solutions of 4 × 10⁻⁴ M in 1(4) were irradiated, and the yields obtained were standardized by use of the value of flugide⁴¹ (0.20 at 313-nm irradiation in toluene) for the photoisomerization.

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