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PHOTOINDUCED INTRAMOLECULAR SUBSTITUTION—III[1]

PHOTOCYCLIZATION OF ω-ANILINOALKYL m-NITROPHENYL ETHERS

KIYOSHI MUTAI* and KEIJI KOBAYASHI

Department of Chemistry, College of Arts and Sciences, The University of Tokyo, Komaba, Meguro-ku, Tokyo 153, Japan

and

KENJI YOKOYAMA

The Institute of Physical and Chemical Research, Wako, Saitama 351, Japan

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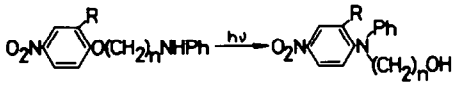
Abstract—Irradiation of 1-(m-nitrophenoxy)-ω-anilinoalkanes, m-$O_2NC_6H_4O(CH_2)_nNHPh$ (n = 2 and 3) and their 1-(2-methoxy-5-nitrophenoxy) analogs induced intramolecular cyclization in which a hydrogen or methoxyl group at the para position with respect to the nitro group is replaced. Although the replacement of the meta Ar–O bond attached to the polymethylene chain was expected by the analogy with intermolecular photosubstitution, no such product was detected. Several reaction features and laser flash study suggests that a radical ion pair formed through photoinduced electron transfer mechanism is involved at the initial stage of the reactions.

Photoinduced aromatic nucleophilic substitution has been characterized by meta-favoring orientation of electron-withdrawing substituents such as nitro and cyano groups.[2] However photoinduced intramolecular substitution of 1-(p-nitrophenoxy)-ω-anilinoalkanes (**1a**) and their 1-(2-methoxy-4-nitrophenoxy) analogs yields N-(p-nitrophenyl)- and N-(2-methoxy-4-nitrophenyl)-ω-anilino-1-alkanols (**2a** and **2b**), respectively, indicating para-favoring orientation of the nitro group.[1,3] The products **2** are the same as those obtained by base-catalyzed rearrangement (the Smiles rearrangement) of **1**. Yokoyama *et al.*[4] have studied the mechanism of the photoreaction of **1** by means of laser flash photolysis and concluded that the reaction is initiated by electron transfer from the anilino to the nitrophenoxy moieties. A radical ion pair thus formed combines to form a spiro-Meisenheimer complex which decomposes to a rearranged product under the catalysis of base.

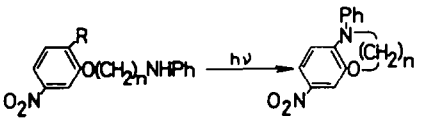


1a, R=H
1b, R=OMe

2a, R=H
2b, R=OMe

We have also studied the photoreaction of m-nitrophenoxy analogs of **1a**, 1-(m-nitrophenoxy)-ω-anilinoalkanes (**3a**), and obtained **4** as a sole isolable product.[5] Thus the para-directing effect of the nitro group has been encountered again in these m-nitrophenyl ethers.

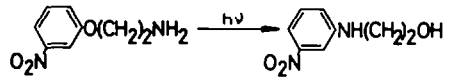
Recently Wubbels *et al.* have reported that 1-(m-nitrophenoxy)-2-aminoethane (**5**), an aliphatic



3a, R=H
3b, R=OMe

4, n=2 and 3

amino analog of **3a**, gives a rearranged product **6** on irradiation.[6] They also have ascertained that the p-nitro analog of **5** gives, along with others, a cyclized



5 **6**

product which results from attack of the amino group at the meta position to the nitro group. Therefore, in the photoinduced reactions of these aliphatic amino derivatives, the nitro group reveals meta-directing effect, just as in intermolecular photosubstitutions.

The object of the present study is to elucidate the mechanism operating in these photoreactions. For this purpose we prepared two types of amino ethers **3a** and **3b** (n = 2–4) and studied their photochemical behavior.

Hereafter **3a** and **3b** are called meta series, according to the relative position of nitro and $-O(CH_2)_n-$ groups, when it is necessary to distinguish them from **1a** and **1b** which could be called para series from the same viewpoint.

Photoreaction of 3

Homologous series of **3a** (n = 2–4) were irradiated in acetonitrile or methanol at 313 nm (high-pressure

Hg lamp). The reaction proceeded with development of yellow color in the solution, which originated from new absorption at *ca* 400 nm. Photoreaction of **3b** (n = 2–4) under the same conditions proceeded in a similar manner. The n = 4 homologs of both **3a** and **3b** showed a slight increase in the intensity of the same region, but no absorption peak or shoulder appeared after more than ten hours of irradiation and no product was isolated.

Usual workup and separation of the reaction mixtures of **3a** (n = 2 and 3) by column chromatography gave heterocyclic compounds **4** as yellow crystals. Structures of **4** (n = 2 and 3) were assigned on the basis of elemental analysis as well as following spectral properties; the ^{1}H NMR spectrum of the product showed disappearance of one proton from the aromatic ring of the starting material **3a**, and resonance pattern in the aromatic region was an ABX type. Concurrent loss of N–H hydrogen was confirmed by NMR and IR spectroscopies. Furthermore, a strong absorption at *ca* 400 nm should be best interpreted as a p-nitroaniline type chromophore.

The products of the n = 2 and n = 3 homologs of **3b** were proved to be the same as those obtained respectively from the corresponding homologs of **3a** by comparison of m.p. and spectral characteristics.

Kinetic study

In order to obtain an insight into the mechanism of this photocyclization, reaction rate was determined. Since the starting materials, **3a** and **3b**, have practically no absorption at around 400 nm and the products **4** exhibit strong peaks in the same region, absorbance increase in this region was used for the determination of the rate. The data for **3a** and **3b** are summarized in Tables 1 and 2, respectively.

The reactions were of first-order. Relative rate constants both for **3a** and **3b** follow the order $n = 2 > 3 \gg 4$. Among the compounds studied, the n = 2 homolog of **3b** exhibited extraordinary fast reaction. Since such a fast reaction was difficult to follow by means of flow-cell procedure, only approximate values for the rate constants could be estimated from the half-lives. The rate accelerating effect of the methoxyl group is undoubtedly due to its being a good leaving group, but it is notable that the effect is limited only to this lowest homolog and the n = 4 homolog still remains inert.

Since base catalysis has been reported for the photoreaction of the para series[1,3] and **5**[7] we carried out the reaction of **3a** in the presence of triethylamine. As shown in Table 1, the rate constants are unexpectedly reduced. The reason for this rate reduction is mainly due to the direct reaction of the nitrobenzene moiety with the amine.[3,8] Generally it is probable that the product of side reaction interferes the determination of reaction rate, but in this case the product shows an absorption peak around 280 nm and gives only negligible effect on the absorption at *ca* 400 nm.

Laser flash study

In order to identify the structure of the reaction intermediate, transient specta of the solution irradiated with N_2 laser were determined. The time dependence of the transient absorption is shown in Fig. 1. The curve indicates two species with lifetimes of *ca* 50 ns (A species) and of *ca* 20–30 μs (B species). One of the most probable species for A is a radical ion pair produced by intramolecular electron transfer from the anilino to m-nitrophenoxy groups, as is the case for the para series. A transient spectrum observed after 10 ns of excitation is shown in Fig. 2 along with a spectral curve obtained by superposing

Table 1. Relative rate constant (k_{rel}) of the photocyclization of **3a**

Solvent	k_{rel} n=2	3	4
CH_3CN	29	19	ca. 0
$CH_3CN + Et_3N$[a]	1	3	
CH_3OH	1.0[b]	1	ca. 0

[a] Concentration, 2.84×10^{-2} mol/l.
[b] Relative k's were determined on the basis of this value.

Table 2. Relative rate constants (k_{rel}) of the photocyclization of **3b**

Solvent	k_{rel} for n=2	3	4
CH_3CN	>700[a]	7	ca. 0
CH_3OH	>500[a]	1[b]	ca. 0

[a] Estimated from the half-life.
[b] Relative k's were determined on the basis of this value.

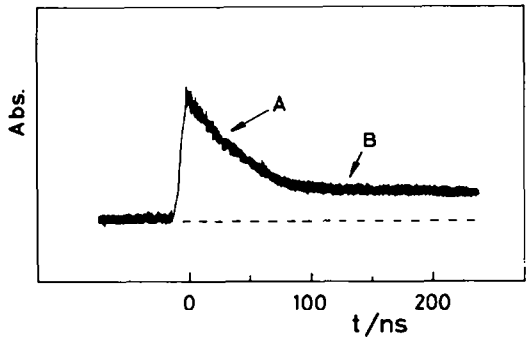


Fig. 1. Time profile of transient absorption of **3a** (n = 2) at 450 nm in EtOH.

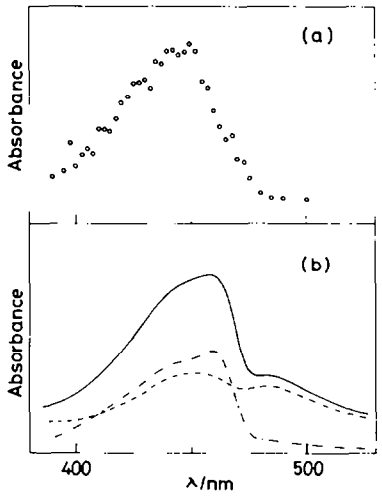


Fig. 2. (a) Transient absorption of **3a** (n = 2) in EtOH (after 10 ns of excitation). (b) Superposed spectrum (———) of m-nitroanisole radical anion(– – – –) and N-ethylaniline radical cation (–·–·–·–).

those of m-nitroanisole radical anion and N-ethylaniline radical cation.[9] The shapes of these two curves resemble each other fairly well and the peaks are nearly at the same position (the difference could be explained in terms of solvent and temperature effects). However, closer inspection of the curves indicates a slight difference in the region beyond 470 nm; the curve in Fig. 2(a) shows a shoulder in this region, but the observed intensities in Fig. 2(b) suggest a smooth curve. Since absorption intensity observed in this region is very low, it is difficult to distinguish whether the difference is due to the instrumental or intrinsic for this intermediate. The transient spectrum of A species (Fig. 2a) resembles that of the cationic component in Fig. 2(b), and it may be argued that laser excitation merely expelled an electron into solvent from the anilino moiety. However, under the conditions where a solution with an absorption maximum at 292 nm in a polar solvent was irradiated at 337 nm (N_2 laser) at room temperature, it is least possible that the anilino group is solely ionized and a resulting cation survives after 10 ns of the irradiation. The structure of A species is likely to be the radical ion pair as expected, but the conclusion is not quite unequivocal so far as it is based merely on the transient spectrum.

As for the structure of B species, the transient absorption exhibited an apparently broad and flat maximum at 400–500 nm and no notable feature is discernible. Thus no further effort to identify this species has been made.

DISCUSSION

From the results obtained for the para **1** and meta **3** series, it has been established that the photosubstitution by anilino group on nitrophenoxy moiety occurs regioselectively at the para position with respect to the nitro group. Superficially, this regioselectivity is in accord with that observed in aromatic nucleophilic substitutions, but this does not necessarily lead to the conclusion that the anilino group plays a role of nucleophile. Indeed it is least possible that a weak nucleophile such as anilino group replaces a hydrogen atom, no matter how strongly the hydrogen is activated by an electron-withdrawing substituent. Furthermore, if the group is excited, its nitrogen atom becomes less nucleophilic and less basic than in the ground state.[10] Thus it is most proabable that the nitrophenoxy group participates in the processes of inducing the substitution and determining the reaction centers in both reacting moities. For instance, in the para series, the anilino group is transformed into a radical cation, acting as an electrophile in the following radical recombination.[4]

Since the same regioselectivity is observed for both series, it may not be irreasonable to suppose that a similar reaction mechanism is operating in the meta series. We can cite some supporting evidences for this reasoning. (i) Laser flash study revealed the presence of a short-lived species whose spectral curve is consistent with that of a supposed radical ion pair, especially in the region around the peak where unambiguous data have been obtained. (ii) Radical ions observed in the para series are formed through electron transfer from anilino to p-nitrophenoxy groups. This process is also possible in the meta series which has a similar donor–acceptor pair. (iii) In radical anions of both p- and m-nitrophenyl ethers, free electron density on the para carbon atom is higher than that on the meta to the nitro group.[11] Thus the observed regioselectivity is consistently explained by the radical ion pair recombination mechanism. (iv) Introduction of methoxyl group greatly enhances the reaction rate (Table 2), and the effect can be attributed to the fact that the substituent is a better leaving group than hydrogen. This phenomenon suggests that the methoxyl group leaves as methoxide anion, which in turn indicates that the nitroaromatic ring is negatively charged at the time of the completion of cyclization, or that the aromatic ring undergoes substitution with a negatively charged or strongly nucleophilic species. Since the latter process is unlikely as has been discussed above, there must be operating a mechanism which generates a nitroaromatic anion. Our mechanism is consistent with this requirement.

There remains an experimental finding which should be explained by this mechanism; that is, why addition of triethylamine is ineffective or even in-

hibitory in the photoreaction of **3a** in contrast to **1**. Though there are insufficient data available, it might be argued that the base actually catalyzes the reaction, but the side reaction of the amine with the nitrophenoxy moiety is very fast to overcome the cyclization reaction, resulting in apparent reduction of the rate. Decelerating effect of the amine has also been noted in the photorearrangement of the n = 4 homologs of both **1a** and **1b**.[1,3] Interestingly, common to these homologs and the meta series is the fact that the rate reduction has been observed in those compounds which show substantial reactivity even in the absence of the amine, though it is yet uncertain whether this phenomenon is inherent in the reaction.

It might also be argued that the process following electron transfer in the meta series is different from that of the para series in which proton abstraction from the positively charged anilino nitrogen in a spiro-Meisenheimer complex is the key step of base-catalysis. Unfortunately the presence of a σ complex to be formed at the time of radical ion recombination could not be ascertained. However, this does not necessarily indicate the absence of the complex, because, if it really exists the lifetime might be in the order less than nano second and cannot be detected by our apparatus or because its concentration may be very low and the spectrum is submerged in the instrumental noise.

Thus we can safely conclude that the photocyclization of the meta series proceeds through a radical ion pair formed by photoinduced electron transfer.

In connection with this mechanism, the remarkable difference between **3** and **5** may deserve comments. Since the para orientation observed in **3** is originated from electron transfer process, we can suppose that the meta-favoring orientation of the nitro group in **5** is due to the absence of this process. As has been pointed out by Wubbels *et al.*[7] an aliphatic amino moiety has a higher ionization potential than an anilino moiety (for instance, ionization potentials for methylamine and N-methylaniline are 9.64 and 7.65 eV, respectively). Thus the meta orientation in the photorearrangement of **5** is probably the consequence of the process lacking electron transfer, i.e. S_N2 Ar* mechanism in the term defined by Havinga *et al.*[13]

EXPERIMENTAL

^{1}H NMR spectra were recorded on JEOL C-60HL and MH-100 spectrometers. The chemical shifts are in ppm with TMS as an internal standard. Electronic spectra were recorded on Hitachi EPS-3T and 100-50 spectrophotometers. All m.ps are uncorrected.

Kinetics of the photoreaction. The rate constants were determined as described in the previous paper.[3] Acetonitrile (Wako, G. R. grade) used for the solvent was distilled from phosphorus pentoxide. Methanol (Wako, G. R. grade) was used after distillation.

Transient absorption measurement. The transient absorption spectra were determined as described previously.[4a]

Materials. 2-Methoxy-5-nitrophenol was prepared by the procedure of Drake *et al.*[14]

1-(*m-Nitrophenoxy*)-ω-*halogenoalkanes.* These compounds, unless otherwise described, were synthesized by the reaction of a corresponding dichloro-alkane or dibromo-alkane with m-nitrophenol as has been reported.[15]

1-(*m-Nitrophenoxy*)-2-*bromoethane.* This compound was obtained in 52% yield as pale yellow liquid; b.p. 145–147°/0.7 mmHg; NMR ($CDCl_3$) δ3.71 (t, 2H, J = 6 Hz), 4.44 (t, 2H, J = 6 Hz), 7.2–8.0 (m 4H). (Found: C, 38.93; H, 3.34; N, 5.63. Calc for $C_8H_8NO_3Br$: C, 39.05; H, 3.28; N, 5.69%.)

1-(*m-Nitrophenoxy*)-3-*bromopropane.* This compound was obtained in 60% yield as pale yellow liquid; b.p. 155–156° 0.7 mmHg. NMR ($CDCl_3$) δ2.19 (m, 2H, C–CH_2–C), 3.67 (t, 2H, J = 6 Hz, CH_2Br), 4.27 (t, 2H, OCH_2), 7.2–8.0 (m, 4H). (Found: C, 41.67; H, 3.85; N, 5.25. Calc for $C_9H_{10}NO_3Br$: C, 41.56; H, 3.88; N, 5.39%.)

1-(*m-Nitrophenoxy*)-4-*bromobutane.* This compound was obtained in 39% yield as pale yellow solid; b.p. 167–172°/1.2 mmHg; m.p. 31–32°; NMR ($CDCl_3$) δ2.0 (m, 4H, C–CH_2CH_2–C), 3.72 (t, 2H, J = 6 Hz, CH_2Br), 4.17 (t, 2H, OCH_2), 7.2–8.0 (m, 4H). (Found: C, 43.87; H, 4.56; N, 4.98. Calc for $C_{10}H_{12}NO_3Br$: C, 43.87; H, 4.41; N, 5.11%.)

1-(2-*Methoxy*-5-*nitrophenoxy*)-2-*bromoethane.* This compound was obtained by the same procedure applied to m-nitrophenoxy analog in 32% yield as colorless crystals; m.p. 128–129°; NMR ($CDCl_3$) δ3.79 (t, 2H, J = 6 Hz, CH_2Br), 4.04 (s, 3H, OCH_3), 4.51 (t, 2H, J = 6 Hz, OCH_2), 7.04 (d, 1H, J = 8 Hz), 7.86 (d, 1H, J = 3 Hz), 8.02 (dd, 1H, J = 3 and 8 Hz). (Found: C, 39.10; H, 3.56; N, 5.04. Calc for $C_9H_{10}NO_4Br$: C, 39.15; H, 3.65; N, 5.07%.)

1-(2-*Methoxy*-5-*nitrophenoxy*)-3-*chloropropane.* To 5.1 g (30 mmol) of 2-methoxy-5-nitrophenol in 30 ml DMF was added 1.4 g of dispersed NaH (50%) in one portion. After the evolution of hydrogen subsided, 50 ml of acetonitrile was added with stirring and the mixture was warmed to *ca* 60°. At this temperature, 1-bromo-3-chloropropane (7.9 g, 50 mmol) was added in one portion and stirring was continued for 3h. After cooling, precipitates were removed by filtration. The solvent was distilled off *in vacuo*, and the remaining solid purified by chromatography (Al_2O_3–benzene). Pale yellow crystals (4.9 g, 66% yield) were obtained; m.p. 89–90°; NMR ($CDCl_3$) δ2.37 (m, 2H, C–CH_2–C), 3.84 (t, 2H, J = 6 Hz, CH_2Cl), 4.01 (s, 3H, OCH_3), 4.27 (t, 2H, J = 6 Hz, OCH_2), 6.93 (d, 1H, J = 8 Hz), 7.76 (d, 1H, J = 3 Hz), 7.88 (dd, 1H, J = 3 and 8 Hz). (Found: C, 48.76; H, 4.88; N, 5.82. Calc for $C_{10}H_{12}NO_4Cl$: C, 48.49; H, 4.92; N, 5.70%.)

1-(2-*Methoxy*-5-*nitrophenoxy*)-4-*bromobutane.* This compound was prepared in the same procedure as its propane homolog by use of 1,4-dibromobutane in 25% yield; m.p. 68–69°; NMR ($CDCl_3$) δ1.9–2.2 (m, 4H, C–CH_2CH_2–C), 3.71 (t, 2H, J = 6 Hz, CH_2Br), 4.01 (s, 3H, OCH_3), 4.20 (t, 2H, J = 6 Hz, OCH_2), 7.06 (d, 1H, J = 9 Hz), 7.88 (d, 1H, J = 3Hz), 8.05 (dd, 1H, J = 3 and 9 Hz). (Found: C, 43.69; H, 4.65; N, 4.53. Calc for $C_{11}H_{14}NO_4Br$: C, 43.44; H, 4.65; N, 4.61%.)

General procedure for the preparation of 1-*aryl*-ω-*anilinoalkanes.* The typical procedure adopted for the preparation of this series of compounds was described in the preceding paper.[1]

1-(*m-Nitrophenoxy*)-2-*anilinoethane* (**3a**, n = 2). This compound was obtained in 66% yield as yellow crystals; m.p. 82.5–83.5°; UV (CH_3CN) λ_{max} 275sh (ϵ 6700) and 330sh nm (ϵ 2100); NMR ($CDCl_3$) δ3.60 (t, 2H, J = 5 Hz, CH_2N), *ca* 4.1 (s, 1H, NH), 4.27 (t, 2H, J = 5 Hz, OCH_2), 6.8–8.1 (m, 9H). (Found: C, 64.92; H, 5.52; N, 10.70. Calc for $C_{14}H_{14}N_2O_3$: C, 65.10; H, 5.46; N, 10.85%.)

1-(*m-Nitrophenoxy*)-3-*anilinopropane* (**3a**, n = 3). This compound was obtained in 74% yield as dark red liquid; b.p. 209–210°/0.4 mmHg; UV λ_{max} 275sh (ϵ 6500) and 330sh nm (ϵ 2050); NMR ($CDCl_3$) δ2.11 (m, 2H, C–CH_2–C), 3.38 (t, 2H, J = 6 Hz, CH_2CN), 3.82 (s, 1H, NH), 4.17 (t, 2H, J = 6 Hz, OCH_2), 6.6–8.1 (m, 9H). (Found: C, 66.24; H, 6.08; N, 10.24. Calc for $C_{15}H_{16}N_2O_3$: C, 66.15; H, 5.92; N, 10.29%.)

1-(*m-Nitrophenoxy*)-4-*anilinobutane* (**3a**, n = 4). This compound was obtained in 84% yield as orange-red crystals; m.p. 51.5–52.5°; UV (CH_3CN) λ_{max} 275sh (ϵ 6500) and 330 nm (ϵ 2000); NMR ($CDCl_3$) δ1.88 (m, 4H, C–CH_2CH_2–C), 3.17 (t, 2H, J = 6 Hz, CH_2CN), 3.66 (s, 1H,

NH), 4.02 (t, 2H, J = 6 Hz, OCH_2), 6.5–7.9 (m, 9H). (Found: C, 67.25; H, 6.48; N, 9.66. Calc for $C_{16}H_{18}N_2O_3$: C, 67.11; H, 6.34; N, 9.78%.)

1-(2-*Methoxy*-5-*nitrophenoxy*)-2-*anilinoethane* (**3b**, n = 2). This compound was obtained in 68% yield as yellow crystals; m.p. 99.5–101°; UV(CH_3CN) λ_{max} 300 (ϵ 7600) and 341 nm (ϵ 7100); NMR (DMSO–d_6) δ3.40 (s, 1H, NH), 3.57 (t, 2H, J = 6 Hz, CH_2CN), 3.95 (s, 3H, OCH_3), 4.30 (t, 2H, J = 6 Hz, OCH_2), 6.6–7.5 (m, 6H), 7.90 (d, 1H, J = 3 Hz), 8.02 (dd, 1H, J = 3 and 9 Hz). (Found: C, 62.45; H, 5.60; N, 9.70. Calc for $C_{15}H_{16}N_2O_4$: C, 62.49; H, 5.59; N, 9.72%.)

1-(2-*Methoxy*-5-*nitrophenoxy*)-3-*anilinopropane* (**3b**, n = 3). This compound was obtained in 54% yield as pale yellow crystals; m.p. 88–89°; UV (CH_3CN) λ_{max} 300 (ϵ 7700) and 342 nm (ϵ 7200); NMR ($CDCl_3$) δ2.20 (m, 2H, C–CH_2–C), 3.43 (t, 2H, J = 6 Hz, CH_2N), 4.03 (s, 3H, OCH_3), *ca* 4.1 (s, 1H, NH), 4.27 (t, 2H, J = 6 Hz, OCH_2), 6.6–7.5 (m, 6H), 7.88 (d, 1H, J = 3 Hz), 8.05 (dd, 1H, J = 3 and 9 Hz). (Found: C, 63.78; H, 5.94; N, 9.27. Calc for $C_{16}H_{18}N_2O_4$: C, 63.57; H, 6.00; N, 9.27%.)

1-(2-*Methloxy*-5-*nitrophenoxy*)-4-*anilinobutane* (**3b**, n = 4). This compound was obtained in 47% yield as yellow crystals; m.p. 94–95°; UV (CH_3CN) λ_{max} 302 (ϵ 7500) and 342 nm (ϵ 7400); NMR ($CDCl_3$) δca 1.9 (m, 4H, C–CH_2CH_2–C), 3.28 (t, 2H, J = 6 Hz, CH_2N), *ca* 3.7 (br s, 1H, NH), 3.98 (s, 3H, OCH_3), 4.18 (s, 2H, J = 6 Hz, OCH_2), 6.6–7.5 (m, 6H), 7.87 (d, 1H, J = 3 Hz), 8.03 (dd, 1H, J = 3 and 9 Hz). (Found: C, 64.27; H, 6.44; N, 8.81. Calc for $C_{17}H_{20}N_2O_4$: C, 64.54; H, 6.37; N, 8.85%.)

7-*Nitro*-4-*phenyl*-2,3-*dihydro*-1,4-*benzoxazine* (**4**, n = 2). Preparative Scale: a soln of 520 mg (2 mmol) of **3a** (n = 2) in 700 ml of acetonitrile under nitrogen was irradiated with a 100W high-pressure Hg lamp through a Pyrex filter and $NiSO_4$ for seven days. After usual workup, the reaction mixture was separated by column chromatography (silica gel-benzene) to give 312 mg (61% yield) of yellow crystals; m.p. 87–87.5°; UV (95% EtOH) λ_{max} 258 (ϵ 6900) and 401 nm (ϵ 17500); NMR ($CDCl_3$) δ3.96 (m, 2H), 4.55 (m, 2H), 6.85 (d, 1H, J = 8 Hz), 7.2–7.55 (m, 5H), 7.66 (dd, 1H, J = 2 and 8 Hz), 7.84 (d, 1H, J = 2 Hz). (Found: C, 65.64; H, 4.69; N, 10.87. Calc for $C_{14}H_{12}N_2O_3$: C, 65.62; H, 4.72; N, 10.93%.)

8-*Nitro*-5-*phenyl*-2,3,4,5-*tetrahydro*-1,5-*benzoxazepine* (**4**, n = 3). This compound was prepared from **3a** (n = 3) by a similar procedure (ten days of irradiation) applied to the n = 2 homolog in 54% yield; m.p. 84–85°; UV (95% EtOH) λ_{max} 262 (ϵ 10500) and 405 nm (ϵ 13500); NMR ($CDCl_3$) δ2.12 (m, 2H, C–CH_2–C), 4.03 (t, 2H, J = 6 Hz, CH_2N), 4.36 (t, 2H, J = 6 Hz, CH_2O), 6.94 (d, 1H, J = 10 Hz), 7.1–7.5 (m, 5H), 7.76 (dd, 1H, J = 3 and 10 Hz), 7.91 (d, 1H, J = 3 Hz). (Found: C, 66.60; H, 5.15; N, 10.09. Calc for $C_{15}H_{14}N_2O_3$: C, 66.60; H, 5.22; N, 10.36%.)

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