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Sensitized ring-opening reactions of 3-(1-naphthyl)-2-(1-naphthalenemethyl)oxaziridine

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Abstract

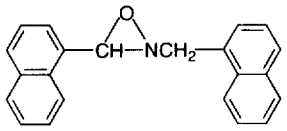
The benzophenone (BP)-sensitized photolysis of the title compound (**1**) in oxygen-free acetonitrile and benzene gave 1-naphthaldehyde and *N*-(1-naphthoyl)-1-naphthalenemethylamine as main products along with small amounts of unidentified products. The occurrence of triplet–triplet energy transfer between BP and **1** at the diffusion-limited rate suggests the participation of triplet **1**, from which the N–O bond cleavage as well as the N–O and C–N bond fissions in the three-membered ring proceeds to eventually yield the amine and the aldehyde, respectively. Control experiments using 1-naphthalenemethylazide showed the involvement of a triplet nitrene intermediate in appearance of the latter product. On the other hand, the 9,10-dicyanoanthracene (DCA)-sensitized reaction of **1** in nitrogen-purged acetonitrile was found to occur by an electron-transfer mechanism giving the product distribution that is different from that of the BP-sensitized reaction. No occurrence of the reaction in benzene confirms that the dissociated oxaziridine cation radical is a precursor of the products obtained. Significantly, the electron-transfer sensitization of **1** in acetonitrile afforded 1-(nitromethyl)naphthalene as one of the products, being consistent with the mechanism in which atomic oxygen derived from the deoxygenation of the nitrone cation radical is captured by the nitrene intermediate. However, the deoxygenation reaction was not observed in methanol where only the aldehyde was detected. This interesting result was explained in terms of solvent effects on the stability of the oxaziridine cation radical as well as of the nitrene cation radical that was generated by the ring-opening reaction of the former cation radical.

Keywords: Sensitized photolysis; Naphthyl-substituted oxaziridine; Energy transfer; Electron transfer; Solvent effects

1. Introduction

Both acyclic and cyclic nitrones photoisomerize readily to the corresponding oxaziridines which in many cases are stable enough to isolate [1]. Lower stability of oxaziridines as compared to other three-membered ring compounds have made extensive studies on their photochemistry somewhat difficult. Introduction of various types of substituents into an oxaziridine ring has permitted the observation of interesting photoreactions of substituted oxaziridines [2–14].

On the other hand, there are only a few studies regarding the photosensitized fragmentation reactions of oxaziridines [5,10,11]. Thus, the mechanism of photofragmentation of an oxaziridine ring is still obscure. In order to shed some light on this mechanism, we prepared 3-(1-naphthyl)-2-(1-naphthalenemethyl)oxaziridine (**1**) and investigated solvent effects on the product distribution derived from benzophenone (BP)- and 9,10-dicyanoanthracene (DCA)-sensitized photolyses of the oxaziridine **1**.



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2. Experimental details

2.1. Measurements

Infrared (IR) and nuclear magnetic resonance (NMR) spectra were taken with a Hitachi 270-30 infrared spectrometer and a JEOL JNM-500 spectrometer, respectively. Chemical shifts of NMR signals were determined using tetramethylsilane as an internal standard. Ultraviolet (UV) absorption and fluorescence spectra were recorded on a Shimadzu UV-2200 spectrophotometer and a Shimadzu RF-5000 spectrofluorimeter, respectively. Fluorescence lifetimes were measured under nitrogen with a time-correlated single photon counting apparatus (Horiba NAES-700; excitation

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wavelength = 366 nm; cut-off wavelength = 410 nm). The half-wave oxidation potential of the oxaziridine **1** vs. a saturated calomel reference electrode (SCE) was determined in acetonitrile by cyclic voltammetry on a Hokuto HAB-151 potentiostat/galvanostat connected to a Yokokawa XY recorder. A solution containing **1** at 10^{-3} mol dm^{-3} was prepared in dry acetonitrile with 0.1 mol dm^{-3} tetrabutylammonium perchlorate as a supporting electrolyte.

2.2. Materials and solvents

N,N-bis(1-naphthalenemethyl)hydroxylamine was prepared in 59% yield by treatment of 1-naphthalenemethyl chloride (50 g, 0.28 mol) with hydroxylamine (9.2 g, 0.28 mol) according to the modified method of Jones and Sneed [15] and was purified by recrystallization from ethanol. M.p., 127.5–128.5°C. IR (KBr) ν: 3220 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 4.24 (s, 4H), 5.39 (s, 1H), 7.27–7.90 (m, 14 H).

The oxidation of *N,N*-bis(1-naphthalenemethyl)-hydroxylamine (2.0 g, 6.4 mmol) with yellow mercury(II) oxide (12.8 g, 12.8 mmol) in diethyl ether–acetone [16] gave crude product, recrystallization of which from hexane–ethyl acetate afforded analytically pure *N*-(1-naphthylidene)-1-naphthalenemethylamine *N*-oxide (28% yield). M.p., 144.0–145.5°C. IR (KBr) ν: 1570, 1160 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 5.66 (s, 2H), 7.30–8.18 (m, 14H), 9.48 (s, 1H). ^{13}C NMR ($CDCl_3$) δ: 69.7, 121.4, 123.3, 125.4, 125.5, 125.66, 125.69, 126.4, 126.7, 126.8, 127.4, 128.9, 129.0, 129.1, 129.3, 130.25, 130.29, 130.6, 130.9, 131.9, 133.4, 133.9. Analysis: calculated for $C_{22}H_{17}NO$: C, 84.86%; H, 5.50%; N, 4.50%; found: C, 84.85%; H, 5.25%; N, 4.72%.

The synthesis of 3-(1-naphthyl)-2-(1-naphthalenemethyl)oxaziridine was photochemically accomplished. An acetonitrile solution of *N*-(1-naphthylidene)-1-naphthalenemethylamine *N*-oxide (0.20 g, 0.64 mmol) was irradiated with Pyrex-filtered light under nitrogen. After the completion of the reaction was ascertained by UV spectroscopy, the reaction mixture was concentrated to dryness affording the residual solid, crystallization of which from hexane–acetonitrile allowed us to obtain analytical-grade oxaziridine (35%). M.p., 79.0–81.0°C. IR (KBr) ν: 3046, 1599, 1512 cm^{-1}. ^{1}H NMR (CD_3CN) δ: 4.62 (d, 1H, J = 13.4 Hz), 4.67 (d, 1H, J = 13.4 Hz), 5.63 (s, 1H), 7.42–8.33 (m, 14H). ^{13}C NMR (CD_3CN) δ: 64.4, 80.0, 123.8, 125.3, 125.9, 126.3, 126.6, 127.0, 127.1, 127.4, 127.6, 128.8, 129.5, 129.6, 129.7, 130.7, 131.7, 132.2, 132.9, 133.0, 134.3, 134.8. Analysis: calculated for $C_{22}H_{17}NO$: C, 84.86%; H, 5.50%; N, 4.50%; found: C, 84.81%; H, 5.26%; N, 4.48%.

1-Naphthalenemethyl azide of high purity was obtained in 90% yield as an oily liquid from the nucleophilic substitution of 1-(chloromethyl)naphthalene (0.11 g, 0.63 mmol) by sodium azide (0.060 g, 0.92 mmol) in dimethyl sulfoxide at room temperature [17]. IR (neat) ν: 2100 cm^{-1}. ^{1}H NMR (CD_3CN) δ: 4.83 (s, 2H), 7.48–8.08 (m, 7H).

N-Aroylation of 1-naphthalenemethylamine (1.0 g, 6.4 mmol) with 1-naphthoyl chloride (0.61 g, 3.2 mmol) under usual conditions [18] gave crude *N*-(1-naphthoyl)-1-naphthalenemethylamine, recrystallization of which from ethanol yielded analytically pure sample (74%). M.p., 191.5–192.0°C. IR (KBr) ν: 3240, 1635 cm^{-1}. ^{1}H NMR (CD_3CN) δ: 5.12 (d, 2H, J = 5.8 Hz), 7.36 (t, 1H, J = 5.8 Hz), 7.46–8.29 (m, 14H). Analysis: calculated for $C_{22}H_{17}NO$: C, 84.86%; H, 5.50%; N, 4.50%; found: C, 85.04%; H, 5.64%; N, 4.42%.

1-(Nitromethyl)naphthalene was synthesized in 16% yield by the nitroalkylation of naphthalene (0.30 g, 2.3 mmol) using nitromethane (0.12 g, 2.0 mmol) according to the method of Kurz et al. [19] and was purified by column chromatography over silica gel (70–230 mesh, Merck) using $CHCl_3$–hexane (1:2 v/v) as the eluent. Oily liquid. IR (KBr) ν: 3052, 1539, 1368 cm^{-1}. ^{1}H NMR (CD_3CN) δ: 6.04 (s, 2H), 7.55–8.04 (m, 7H). Analysis: calculated for $C_{11}H_9NO_2$: C, 70.58%; H, 4.85%; N, 7.48%; found: C, 69.95%; H, 4.52%; N, 6.75%.

N-(1-Naphthylidene)-1-naphthalenemethylamine was derived from the condensation reaction between 1-naphthalenemethylamine (0.90 g, 5.9 mmol) and 1-naphthaldehyde (0.93 g, 5.9 mmol) in dry benzene [20] and was recrystallized from ethyl acetate–hexane to give analytically pure sample (73%). M.p., 66.0–68.0°C. IR (KBr) ν: 3004, 2866, 1617 cm^{-1}. ^{1}H NMR (CD_3CN) δ: 5.30 (s, 2H), 7.44–9.06 (m, 14H), 9.10 (s, 1H). Analysis: calculated for $C_{22}H_{17}N$: C, 89.46%; H, 5.80%; N, 4.74%; found: C, 89.29%; H, 5.89%; N, 4.43%.

Acetonitrile and methanol were purified according to the standard method [21]. Benzene was of spectroscopic grade and was used as received.

2.3. Product analysis

For the purpose of determining the structure and yield of photoproducts, an acetonitrile solution (40 cm^3) of the starting oxaziridine (2.0×10^{-4} or 2.0×10^{-3} mol dm^{-3}) containing DCA (2.0×10^{-4} mol dm^{-3}) or BP (2.0×10^{-2} mol dm^{-3}), placed in a Pyrex vessel, was irradiated under nitrogen at room temperature with light of wavelengths longer than 380 nm (DCA, Corning 3–75 glass filter) or 340 nm (BP, Corning 0–52 glass filter) from a 450 W high-pressure Hg lamp. At suitable time intervals an aliquot of the solution was pipetted off and then submitted to UV spectroscopic analysis. After 2-h (BP) or 6-h (DCA) irradiation, the remaining solution was concentrated to dryness and the resulting residue was subjected to ^{1}H NMR analysis or to separation by preparative thin layer chromatography on silica gel (standard grade) using hexane–dichloromethane (1:1 v/v) as the mobile phase. The structure of products was determined by comparing ^{1}H NMR spectra of isolated products with those of independently prepared authentic samples, while the yield was estimated by the area of a given NMR signal for each product relative to that for the internal standard: *N*-(1-naphthylidene)-1-naphthalenemethylamine *N*-oxide that was added just before the NMR measurement of

the product mixture. The same procedure was applied to the product analysis in benzene and methanol. Comparison of isolated and ^{1}H NMR yields showed that the former yield is lower than the latter by 5–10%. This must be due to loss of a given product in the course of its isolation procedure.

3. Results and discussion

3.1. Emission quenching of BP and DCA by 1

As shown in Fig. 1, the room-temperature phosphorescence of BP (the first singlet excitation energy, $E_S = 311$ kJ mol^{-1}; the first triplet excitation energy, $E_T = 289$ kJ mol^{-1}) [22] was efficiently quenched by **1**, whose excitation energies may be approximated by those ($E_S = 377$ kJ mol^{-1}; $E_T = 254$ kJ mol^{-1}) of 1-methylnaphthalene [22], according to the Stern–Volmer equation (Eq. (1)):

$$I_0/I = 1 + k_q \tau_T [\mathbf{1}] \quad (1)$$

where I and I_0 are the emission intensities of BP with and without **1** in acetonitrile, respectively, k_q is the bimolecular quenching rate constant and τ_T is the BP-phosphorescence lifetime (26 μs) [23] in the absence of **1**. From the slope of this linear plot, k_q was estimated to be 6.2×10^9 dm^3 mol^{-1} s^{-1}, indicating the occurrence of nearly diffusion-limited phosphorescence quenching. Although exothermic triplet–triplet energy transfer between BP and **1** is very likely to be responsible for the observed emission quenching, there remains the possibility of contribution of an electron-transfer mechanism to the overall quenching process. In order to examine this possibility, the free-energy change (ΔG) for electron transfer from **1** to triplet BP was calculated based on the simplified Weller equation (Eq. (2)) [24,25]:

$$\Delta G/\text{kJ mol}^{-1} = 96.5[E_{ox} - E_{red}] - E_T (\text{or } E_S). \quad (2)$$

where E_{ox} and E_{red} refer to the oxidation potential of **1** (+1.3 V vs. saturated calomel electrode, SCE in MeCN) and the reduction potential of BP (−1.83 V vs. SCE in MeCN) [26], respectively. The calculated ΔG value of +13 kJ mol^{-1} suggests the minor contribution of electron-transfer emission quenching. Thus, the magnitude of the quenching rate constant demonstrates that an energy-transfer mechanism operates predominantly in the phosphorescence quenching of BP.

An analysis of the plot shown in Fig. 2 reveals that **1** also quenches the DCA (excited singlet-state lifetime, $\tau_S = 16.0$ ns) fluorescence following the Stern–Volmer equation to give the quenching rate constant (k_q) of 1.9×10^{10} dm^3 mol^{-1} s^{-1}. In addition to highly endothermic singlet–singlet energy transfer between DCA ($E_S = 279$ kJ mol^{-1}; $E_{red} = -0.98$ V vs. SCE in MeCN) [27] and **1** ($E_S = 377$ kJ mol^{-1}), the ΔG value of −59 kJ mol^{-1} for electron transfer from the ground-state **1** to singlet DCA confirms that the observed fluorescence quenching takes place by an electron-transfer mechanism.

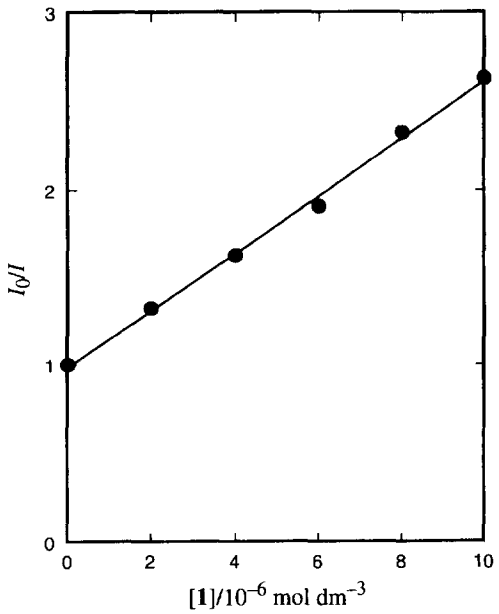


Fig. 1. Stern–Volmer plot for the phosphorescence quenching of BP (2.0×10^{-2} mol dm^{-3}) by **1** in oxygen-free acetonitrile at room temperature. Excitation wavelength, 366 nm.

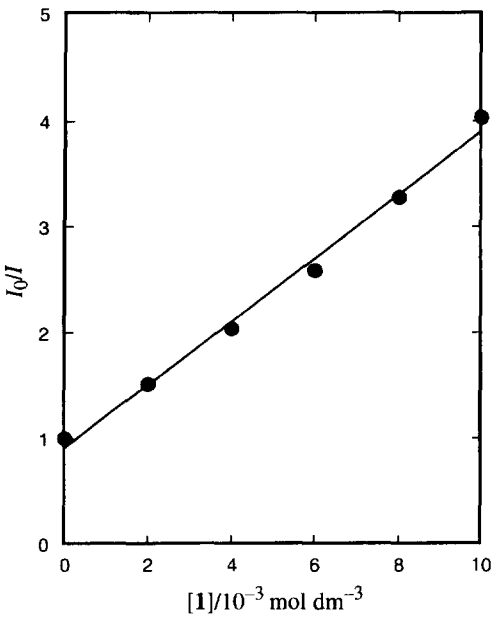
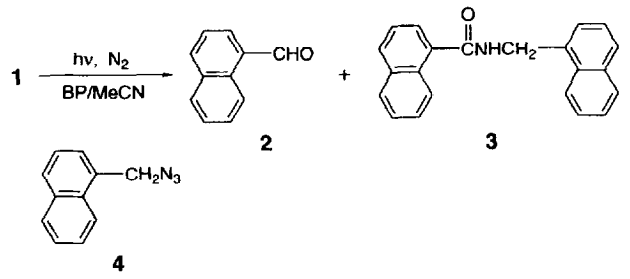


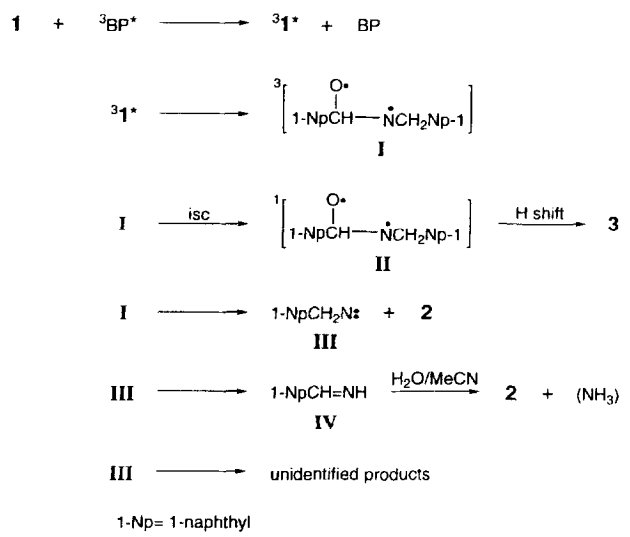
Fig. 2. Stern–Volmer plot for the fluorescence quenching of DCA (1.0×10^{-4} mol dm^{-3}) by **1** in nitrogen-saturated acetonitrile at room temperature. Excitation wavelength, 366 nm.

3.2. BP-sensitized photolysis

As shown in Scheme 1, irradiation of a nitrogen-purged acetonitrile solution of **1** (2.0×10^{-3} mol dm^{-3}) containing BP (2.0×10^{-2} mol dm^{-3}) with light of wavelengths longer than 340 nm (>340 nm) for 2 h at room temperature gave 1-naphthaldehyde (**2**; 59% yield) and *N*-(1-naphthoyl)-1-naphthalenemethylamine (**3**; 26%) along with small amounts of unidentified products. The BP concentration remained constant throughout the irradiation period (UV



Scheme 1.



Scheme 2.

analysis). Splitter and Calvin [5] have shown that triplet oxaziridine undergoes photofragmentation to afford aldehyde and triplet nitrene-derived products whereas amide is obtained by rearrangement of singlet oxaziridine. In addition, the finding that the starting **1** quenches BP phosphorescence at the rate that is very close to the diffusion-controlled indicates the occurrence of the sensitized decomposition from the triplet excited state, and hence, we are led to propose Scheme 2. If an electron-transfer mechanism contributes to the overall sensitized reaction to a substantial extent, product distribution as well as product yield is predicted to undergo pronounced solvent polarity effects because non-polar solvents have negligible ability to stabilize anion and cation radicals produced by an electron transfer [28,29]. When the BP-sensitized photolysis of **1** (2.0×10^{-4} mol dm^{-3}) was conducted in benzene under the same irradiation conditions, **2** (57% yield) and **3** (24%) were formed in almost the same yields as those estimated in acetonitrile, being consistent with a predominant energy-transfer mechanism (Scheme 2).

Since homolytic N–O bond cleavage is known to readily occur in triplet *N,O*-disubstituted hydroxylamines [30–32], triplet **1** may generate the triplet 1,3-biradical **I** intersystem crossing of which gives **II**, a precursor of **3**, in competition with the C–N bond fission of **I**. This bond fission is considered to result in the nitrene intermediate **III** and **2**. Ab initio calculations of methylnitrene in the triplet ground state and methylimine revealed that the imine is thermodynamically more stable than the nitrene by 42 kJ mol^{-1} [33], and thus there is substantial driving force for the rearrangement to the imine **IV**. Irradiation of 1-naphthalenemethylazide (**4**; 2.0×10^{-3} mol dm^{-3}), which quenched the BP phosphorescence ($k_q=2.6\times10^{9}$ dm^3 mol^{-1} s^{-1}), in oxygen-free acetonitrile containing BP (2.0×10^{-2} mol dm^{-3}) with >340 nm light for 2 h produced the aldehyde **2** in 30% yield together with complicated product mixtures. Any attempts to isolate crystalline products from this mixture were not fruitful. Taking into account that the imine **IV** is hydrolyzed by water as a contaminant yielding **2** and ammonia (isolation of the latter product was not attempted), this observation provides evidence for the participation of the triplet nitrene intermediate.

3.3. DCA-sensitized photolysis

Kawamura et al. [10] and Iwano et al. [11,13] have shown that DCA-sensitized reactions of 3-aryl-2-methyloxaziridines proceed by an electron-transfer mechanism mainly forming aromatic aldehydes whereas geometrically constrained oxaziridines are subject to stereoselective isomerizations to the corresponding nitrones under similar irradiation conditions. Thus, substituents introduced into an oxaziridine ring exert a striking effect on the ring-opening pathway of oxaziridine cation radicals.

The absorption spectral changes that are caused by irradiation of a nitrogen-saturated acetonitrile solution of **1** containing DCA with >380 nm light are shown in Fig. 3. The absorption detected around 320 nm was increased with irradiation, whereas the DCA absorption remained unchanged in the wavelength range 380–450 nm during irradiation. Comparison of ^{1}H NMR spectra of isolated products with those

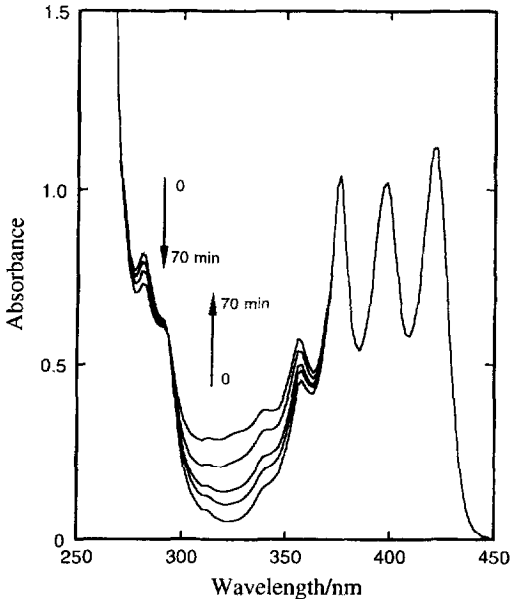
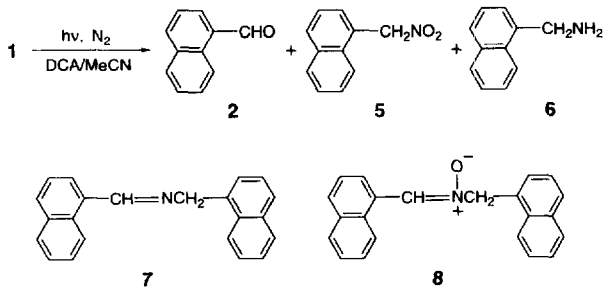
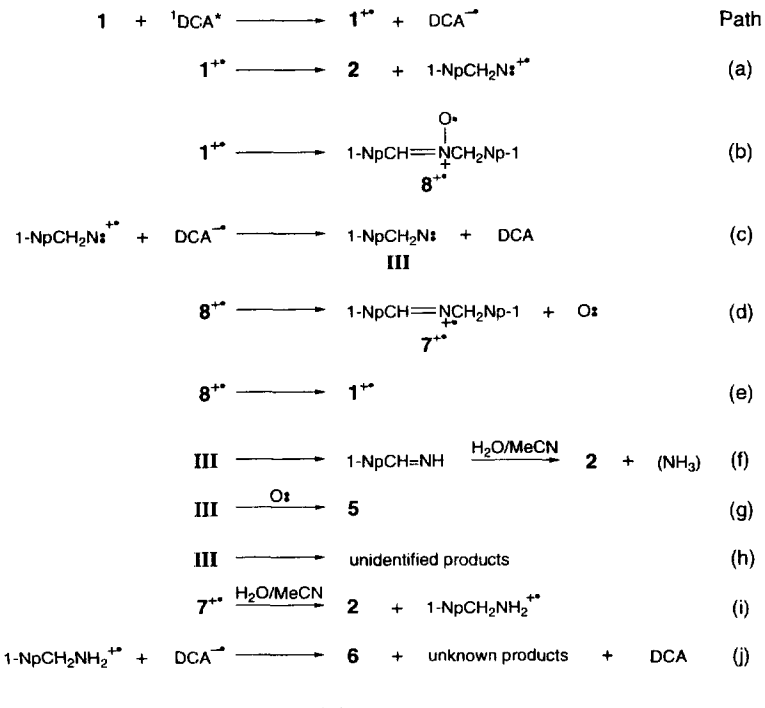


Fig. 3. UV absorption spectral changes during irradiation ($\lambda_{irr}>380$ nm) of **1** (5.0×10^{-5} mol dm^{-3}) in nitrogen-purged acetonitrile containing DCA (1.0×10^{-4} mol dm^{-3}) at room temperature.

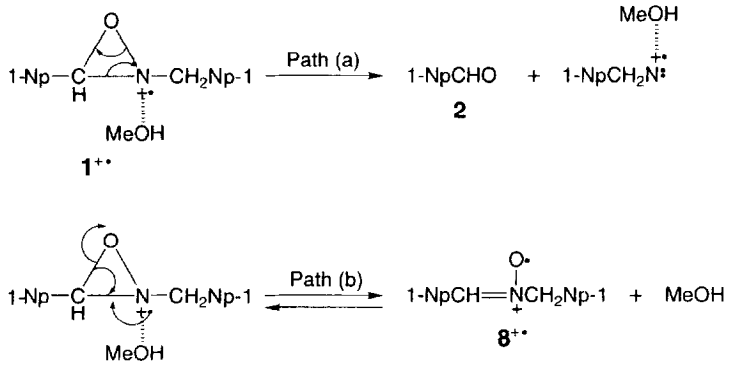


Scheme 3.

of independently prepared authentic samples revealed that the DCA (2.0×10^{-4} mol dm^{-3})-sensitized photolysis of **1** (2.0×10^{-3} mol dm^{-3}) gives **2** (51% yield), 1-(nitromethyl)naphthalene (**5**; 14%) and 1-naphthalenemethylamine (**6**; 7%) along with unidentified products (Scheme 3). The fact that the amine **6** readily decomposes to give unknown products on irradiating an acetonitrile solution of **6** (2.0×10^{-4} mol dm^{-3}) in the presence of DCA (2.0×10^{-4} mol dm^{-3}) offers a good explanation for the much lower yield of this amine than expected. As described in Section 3.2, non-polar solvents have negligible ability to stabilize dissociated cation and anion radicals [28,29], and hence, back electron transfer should preferentially take place within the geminate ion radical pair produced by an electron transfer in these solvents. Not only the ΔG estimated in benzene (ΔG (benzene) = ΔG (MeCN) + 32 kJ mol^{-1} = −27 kJ mol^{-1} [34]) but also the k_q (τ_S = 12.1 ns; $k_q = 9.1\times10^9$ dm^3 mol^{-1} s^{-1}) for the quenching of DCA fluorescence by the oxaziridine **1** in this nonpolar solvent indicates the occurrence of the electron transfer emission quenching that affords caged oxaziridine cation and DCA anion radicals. Therefore, the fact that no sensitized reaction occurs in benzene strongly suggests that back electron transfer exclusively proceeds in the initially-formed geminate ion radical pair to give a negligible amount of the dissociated oxaziridine cation and DCA anion radicals, which must be involved in the reaction process in acetonitrile. In addition to this suggestion, the following observations lead us to propose Scheme 4: (1) the DCA concentration remained constant during irradiation, showing that the DCA anion radical is eventually oxidized to regenerate DCA [Paths (c) and (j)]; (2) the DCA-sensitized photolysis of the azide **4** (2.0×10^{-4} mol dm^{-3}), which induced the DCA-emission quenching ($k_q = 1.2\times10^{10}$ dm^3 mol^{-1} s^{-1}), with >380 nm light in oxygen-free acetonitrile (4-h irradiation) afforded the aldehyde **2** (21% yield) as the only identified product [Paths (c), (f) and (h)]; (3) in addition to a small amount of the amine **6** (<5% yield), the nitromethylnaphthalene **5** (22%) and the aldehyde **2** (52%) were obtained by the independent 4-h irradiation of *N*-(1-naphthylidene)-1-naphthalenemethylamine *N*-oxide (**8**; 2.0×10^{-4} mol dm^{-3}), which has the k_q value of 1.8×10^{10} dm^3 mol^{-1} s^{-1} for the sensitizer-emission quenching, under the same conditions as above [Paths (b), (d), (e), (g), (i) and (j)]; (4) the imine **7** (2.0×10^{-4} mol dm^{-3}), which also quenches the sensitizer fluorescence ($k_q = 1.8\times10^{10}$ dm^3 mol^{-1} s^{-1}), readily underwent hydrolytic cleavage yielding **2** (79% yield) and **6** (10%) under the irradiation conditions used [Paths (i) and (j)]; (5) we were never able to detect the nitro compound **5** upon direct photolysis of the azide **4** (2.0×10^{-4} mol dm^{-3}) in oxygen-saturated acetonitrile [Path (g)].



Scheme 4.



Scheme 5.

The finding that the DCA-sensitized deoxygenation of arylnitrones proceeds through a nitrone cation radical intermediate [10,11] also substantiates Paths (b) and (d) shown in Scheme 4. Kawamura et al. [10] and Iwano et al. [11] have succeeded in isolating one of the deoxygenation product, imine, but failed in detecting another product, possibly nitro compound. The successful isolation of the imine may be due to the more increased stability of their imine cation radical toward hydrolysis, as compared to that of our imine cation radical $\mathbf{7}^{+\cdot}$. The presence of 1 vol.% water exerted only a very small effect on the yield of **2** (51% in MeCN; 55% in MeCN-1 vol.% H_2O) that was obtained by the DCA-sensitized reaction of a relatively low concentration of **1** in acetonitrile, being consistent with the mechanism in which there is no pathway competing with the hydrolytic cleavage of the imine 1-NpCH=NH as well as $\mathbf{7}^{+\cdot}$ by water as a contaminant (Scheme 4). It is likely that a nitrene intermediate is generated also in the sensitized photolysis of 3-aryl-2-methyloxaziridine and its isomeric arylnitrone [10,11] but this nitrene cannot capture atomic oxygen owing to much shorter lifetime than that of 1-naphthalenemethylnitrene (**III**). Since the nitrene **III** reacts with molecular oxygen forming no nitro compound [35], the appearance of **5** in the DCA-sensitized reaction of **1** under nitrogen presents evidence in support of the existence of atomic oxygen. Kawamura et al. [10] and Iwano et al. [11,13] also revealed that substituent groups introduced into an oxaziridine ring control the ease with which interconversion is achieved between the oxaziridine cation radical and its isomeric nitrone cation radical. The 1-naphthyl group may act so as to render the interconversion of $\mathbf{1}^{+\cdot}$ and $\mathbf{8}^{+\cdot}$ (Scheme 4) possible.

Interestingly, the sensitized reaction in methanol, where DCA (1.0×10^{-4} mol dm^{-3}) fluorescence ($\tau_S = 15.6$ ns) was quenched by **1** at the diffusion-limited rate ($k_q = 1.5\times10^{10}$ dm^3 mol^{-1} s^{-1}), gave **2** alone in 39% yield at 47% conversion of the starting **1**. In a previous study [36], it was found that the DCA-sensitized photooxidation of *N*,*N*-dibenzylhydroxylamine occurs by an electron-transfer mechanism and then proceeds in higher quantum yield in methanol than in acetonitrile. This solvent effect on the oxidation efficiency was explained in terms of the additional stabilization of the initially-formed ion radical pair due to solvation in the protic solvent. Comparison of the k_q values estimated in acetonitrile and methanol confirms the exclusive operation of an electron-transfer mechanism also in the latter solvent. It is, thus, very likely that solvation of the oxaziridine cation radical $\mathbf{1}^{+\cdot}$ by methanol affects its bond-cleavage pathway. On irradiation of a nitrogen-purged methanol solution of **8** (2.0×10^{-4} mol dm^{-3}) containing DCA (1.0×10^{-4} mol dm^{-3}) with >380 nm light for 3 h at room temperature, only **2** was detected (yield, 28%; conversion, 30%). Because an electron transfer should be responsible for the quenching of DCA emission by **8** ($k_q = 1.2\times10^{10}$ dm^3 mol^{-1} s^{-1}), the significant result described above demonstrates that the cation radical $\mathbf{8}^{+\cdot}$ is readily converted into $\mathbf{1}^{+\cdot}$ (Path (b) in Scheme 5) from which the aldehyde **2** is derived. The solvation of $\mathbf{1}^{+\cdot}$ by methanol is deemed to increase its thermodynamic stability relative to that of $\mathbf{8}^{+\cdot}$. In addition, the enhanced stability of the nitrene cation radical due to solvation is also a likely driving force that makes Path (a) predominant route.

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