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STEADY-STATE AND NANOSECOND SPECTROSCOPIC STUDIES OF TRIPLET SENSITIZED REACTION OF K-REGION ARENE OXIDES

MICHIYA ITOH,* KENJI MURATA and KUNIHIRO TOKUMURA
Faculty of Pharmaceutical Sciences, Kanazawa University, Takara-machi, Kanazawa 920, Japan

and

KOICHI SHUDO, NAOKI MIYATA and TOSHIHIKO OKAMOTO
Faculty of Pharmaceutical Sciences, The University of Tokyo, Bunkyo-ku Tokyo 113, Japan

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Abstract—Photorearrangement reactions of K-region arene oxides, 9,10-epoxy-9,10-dihydrophenanthrene (**1a**), 3-acetyl-9,10-epoxy-9,10-dihydrophenanthrene (**1b**), and 3,4-epoxy-3,4-dihydropyrene (**1c**) in dichloroethane (DCE) solution were investigated by steady irradiation and nanosecond transient spectroscopy. Photorearrangements producing substituted oxepins, **2** occur via the singlet excited state of these compounds, while the phenolic products, 9-hydroxyphenanthrene (**3a**), 3-acetyl-9-hydroxyphenanthrene (**3b**), and 4-hydroxypyrene (**3c**) are formed via the triplet state. Phenol **3** formation from the triplet **1** sensitized by the triplet **3** (i.e. product sensitization) is proposed for the photorearrangement reactions of **1a** and **1c**, and this process is the only way phenol (**3a**) is formed because of the negligible intersystem crossing probability of **1a**. No product sensitization occurs in the photorearrangement reaction of **1b**.

Numerous investigations of photorearrangement reactions of K-region arene oxides have been reported during the last decade. Shudo and Okamoto[1] noted a significant wavelength dependence on the photorearrangement reaction of 9,10-epoxy-9,10-dihydrophenanthrene (**1a**). Direct irradiation of **1a** at 250–290 nm in dichloromethane solution gives dibenz[b,d]oxepin (**2a**) as the major photoproduct. Griffin *et al.*[2] suggest that **2a** and **3a** are formed via the singlet and triplet excited states of **1a**, respectively, based on the triplet sensitization experiments conducted with benzophenone and triphenylene. Furthermore, they[3] report no oxepin formation occurs upon photolysis of 3-acetyl-9,10-epoxy-9,10-dihydrophenanthrene (**1b**), but 3-acetyl-9-hydroxyphenanthrene (**3b**) is formed by way of the triplet state of **1b** formed through intersystem crossing. Van Duuren[4] proposes that the photorearrangement of 3,4-epoxy-3,4-dihydropyrene (**1c**) leads to tribenz[b,c,d]oxepin (**2c**) and 4-hydroxypyrene (**3c**).

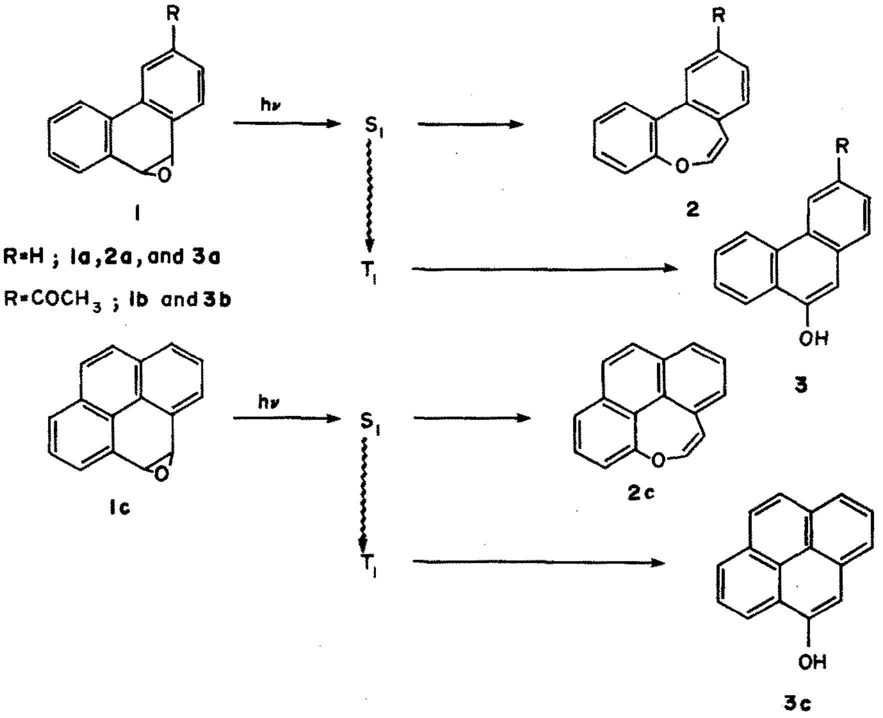
This paper describes steady irradiation and nanosecond spectroscopic studies of the three arene oxides (**1a**, **1b** and **1c**). It is confirmed in these systems that singlet and triplet state mechanisms are operative for oxepin and phenol formation in DCE solution, respectively. Triplet sensitized rearrangement in which phenolic product serves as the sensitizer is proposed for the formation of phenol based on the quenching behavior by oxide against the triplet–triplet (T–T) absorption of phenol. The phenol formation through intersystem crossing from the singlet to the triplet excited state may be neglected in the case of **1a**, but compete with that through product sensitization in the case of **1c**.

In polar solvents such as 2-methyltetrahydrofuran (MTHF) and acetonitrile, however, no triplet energy transfer is observed in the two systems, **3a**–**1a** and **3c**–**1c**. This is attributed to the molecular interaction between phenol and solvent molecules (perhaps due to H-bonding), which appears to stabilize the triplet energy level of phenol to a greater extent than that of the corresponding parent oxide. Neither intersystem crossing of **1a** nor triplet energy transfer from **3a** to **1a** occurs in MTHF. Under these conditions, irradiation for this solution affords only the oxepin, **2a**.

RESULTS AND DISCUSSION

Steady irradiation. An aerated 1,2-dichloroethane (DCE) solution (5×10^{-5} M) of **1a** was irradiated with a monochromatic source (279 nm) at room temperature, and the corresponding spectral changes (Fig. 1b) indicate that the major rearrangement pathway is **1a** to **2a**. A deaerated DCE solution of **1a** was irradiated at 279 nm in the same manner. It is evident from the spectra of this solution shown in Fig. 1(c) that **3a** is formed in quantitative yield under these conditions. These spectral changes demonstrate that **2a** and **3a** are the major photoproducts formed in the aerated and deaerated DCE solutions, respectively. In the previous paper,[1] however, secondary photoreaction accompany the formation of fluorene and a dimer seems to be involved in the aerated dichloromethane solution.

Irradiation (337 nm) of the deaerated DCE solution of **1a** causes very rapid formation of **3a**. Upon excitation at 337 nm, the species initially photoexcited may be **3a** formed in trace amounts as a contaminant in the samples of **1a**, which itself is transparent at 337 nm. A reasonable possibility of this argument is confirmed by observing faster photorearrangement of **1a** upon addition of small amounts of **3a** to the solution. The results in the aerated and deaerated DCE solutions indicate that **2a** is probably formed via the singlet excited state and **3a** through the triplet excited state as previously proposed.[2] The apparent second order reaction kinetics observed in the long wavelength (337 nm) irradiation experiments suggests that **3a** sensitizes the photorearrangement of **1a** to **3a**. Further, biacetyl, an efficient triplet quencher (5×10^{-3} M) added to the deaerated solution of **1a** quenches



the formation of **3a** in a manner similar to that observed with oxygen in aerated solutions. The wavelength dependence of the photorearrangement reaction reported previously[1] may be understood in terms of the reaction sequence described above, in which the phenolic products which absorb at long wavelength sensitize product formation.

Figure 2 shows the changes observed in the absorption spectra of an aerated DCE solution of **1b** during prolonged irradiation (337 nm) at room temperature. The spectral changes indicate that **3b** is formed in almost quantitative yield. Furthermore, upon irradiation of the absorption band (337 nm) of small amounts of **3b** added to the solution of **1b**, no increase in formation of **3b**, i.e. no product sensitization is observed. Griffin *et al.*[3] pointed out that efficient intersystem crossing from the singlet to the triplet excited state could be expected in the case of **1b**. A n→π^* character may be attributed to the lowest

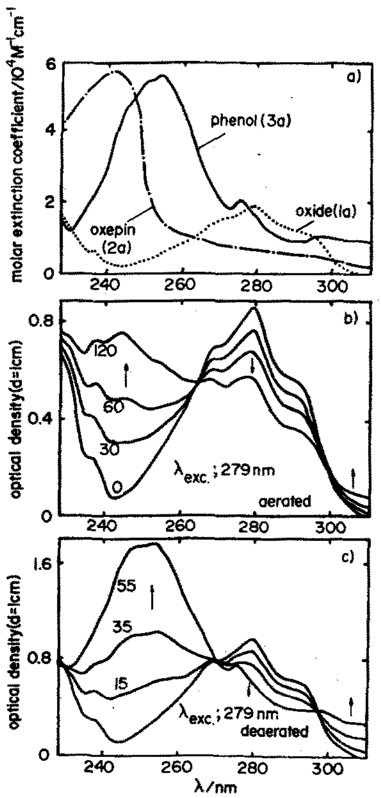


Fig. 1. (a) Absorption spectra of 9,10-epoxy-9,10-dihydrophenanthrene (**1a**) and photo-products (**2a**, **3a**) in DCE. (b) Progressive spectral change of an aerated DCE solution of **1a** with irradiation of 279 nm-light. (c) That of a deaerated DCE solution of **1a** with irradiation of 279 nm-light. Number beside each spectrum is irradiation time in minute.

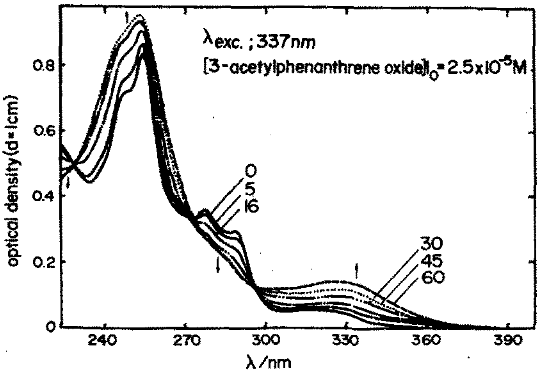


Fig. 2. Progressive spectral change of a deaerated DCE solution of 3-acetyl-9,10-epoxy-9,10-dihydrophenanthrene (**1b**) with irradiation of 337 nm-light. Numbers are irradiation time in minute.

singlet excited state of the epoxy-ketone, **1b**, and intersystem crossing probability appears to be almost unity in accordance with Griffin's predictions.

Irradiation of an aerated DCE solution of **1c** at room temperature indicates formation of **2c**, and the absorption band ($\lambda_{max} = 237$ nm) increases in intensity as **1c** is consumed (Fig. 3b). The quantum yield of oxepin, **2c** formation in DCE was determined to be 0.2. Irradiation of the deaerated solution exhibits formation of **3c** as well as **2c**, as evidenced by the spectral changes shown in Fig. 3(c). Long wavelength (337 nm) irradiation of the deaerated solution of **1c** containing small amounts of **3c** also exhibits triplet sensitization producing **3c** as mentioned above. However, the triplet sensitization (**1c** by **3c**) is less pronounced than that observed between **3a** and **1a**.

The triplet sensitization producing **3a** was not detected in the irradiation (337 nm) of deaerated 2-methyltetrahydrofuran (MTHF) and/or acetonitrile solutions. Absorption spectral changes of this deaerated solution in the excitation of 279 nm as well as 337 nm indicate almost quantitative formation of **2a** and no formation of **3a**. The facts exhibit neither triplet sensitization nor intersystem crossing in the photorearrangement of **1a** in MTHF. No triplet sensitization was also observed in **1c**, though irradiation (264 nm) of the deaerated MTHF solution of **1c** gave **3c** via intersystem crossing. The significant solvent dependence of the triplet sensitization may be attributable to the electronic interaction between phenol and solvent molecule. Absorption spectra of **3a** in several concentrations (10^{-3}–10^{-1} M) of MTHF in heptane show 1; 1 complex formation between **3a** and solvent molecule,[5] and also show red-shift (approximately 800 cm^{-1}) of the first band of **3a**. If triplet energy is stabilized in parallel with that of the singlet state, no triplet sensitization in MTHF may be attributable to the stabilization of the triplet state of **3a** greater than that of **1a**.

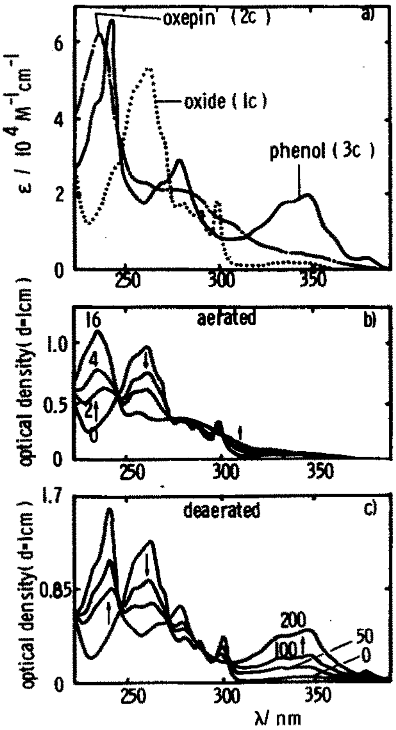


Fig. 3. (a) Absorption spectra of 3,4-epoxy-3,4-dihydropyrene (**1c**) and photo-products (**2c**, **3c**) in DCE. (b) Progressive spectral change of an aerated DCE solution of **1c** with irradiation of 264 nm-light. (c) That of a deaerated DCE solution of **1c** with irradiation of 337 nm light. Numbers are irradiation time in minute.

Nanosecond transient spectroscopy. In order to investigate the **3a** triplet sensitization upon photorearrangement of **1a**, transient absorptions were determined in the aerated DCE solution of **3a** at room temperature by the aid of a nitrogen gas laser and a microsecond Xe flash lamp. The spectrum is shown in Fig. 4. Similar transient absorption band was also observed in an aerated MTHF solution of **3a** at 77°K. The decay time of the transient absorption band (1.5 sec) at 77°K is approximately identical to that of phosphorescence at 510 nm (1.3 sec). Therefore, the transient absorption band at room temperature shown in Fig. 4 may be a triplet–triplet (T–T) absorption band of **3a**. The T–T absorption band is quenched by **1a** added to the solution of **3a**. The concentration dependence (Fig. 4) of decay rate constant of the T–T absorption band affords the quenching rate constant of 2.9×10^7 M^{-1} s^{-1}. The results indicate a triplet energy transfer of **3a** to **1a**, which implies the **3a** triplet sensitization mentioned above. Small quenching rate constant suggests that two triplet energy levels are very close to each other.[6] In the deaerated MTHF solution of **3a** at room temperature, however, the T–T absorption band is not quenched by **1a**, which implies no triplet energy transfer in this solvent. The fact may be consistent with the results of no triplet sensitization in MTHF observed in the steady irradiation. There is a possible formation of **3a** via intersystem crossing. However, no formation of **3a**, but dominant formation of **2a** in the steady irradiation of the deaerated MTHF solution of **1a** suggests that no intersystem crossing occurs in this compound. Usual intersystem crossing cannot depend so much on the solvent system as the triplet energy transfer. Therefore, it seems that intersystem crossing of **1a** is negligible even in DCE. Quantum yield of **2a** formation in aerated DCE solution was determined to be approximately 0.4 at room temperature.

A T–T absorption band of 3-acetyl-9-hydroxy-

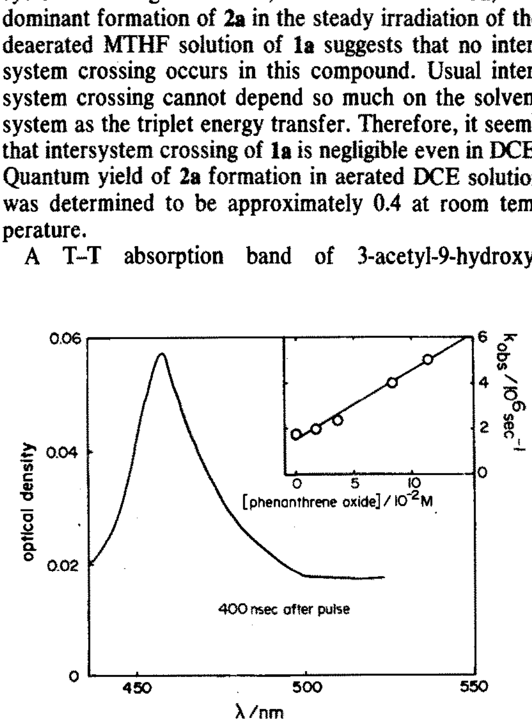


Fig. 4. T–T absorption spectrum at 400 nsec after a laser pulse for an aerated DCE solution of **3a** (6.6×10^{-3} M). An inset shows the plots of apparent decay rate constant of the T–T absorption against the concentration of **1a** added.

phenanthrene (**3b**) in aerated solution of DCE or MTHF was observed in the similar wavelength region to that of **3a**. However, no quenching of the T–T absorption band of **3b** by **1b** added to the aerated DCE solution was detected, which implies no triplet energy transfer of **3b** to **1b**. The results correspond well with no triplet sensitization of **3b** in the rearrangement of **1b** mentioned in the last section. On the other hand, a long-lived transient absorption band ($\lambda_{max} = 395$ nm, $\tau = 650$ nsec) was observed in the aerated DCE solution of **1b**, whose lifetime increases in the deaerated solution. Then, the long-lived absorption band may be ascribed to a T–T absorption band of **1b**, though no phosphorescence was observed. Here, if phenol **3b** is formed via the triplet state of **1b**, rise of an absorption band of **3b** might be observed in the same time constant as a decay time of the T–T absorption. However, no rise of the absorption band of **3b** was observed at this stage, because of a weak absorption (330–370 nm, see Fig. 2) of this compound.

Transient absorption band ($\lambda_{max} = 410$ nm, $\tau = 840$ nsec) in the aerated DCE solution of 4-hydroxypyrene (**3c**) was observed, and ascribed to a T–T absorption band of this compound in the same manner as mentioned above, of which spectrum is shown in Fig. 5. Increase of decay rate constant of the T–T absorption band of **3c** with increasing concentration of **1c**[7] added to this solution was determined to afford a quenching rate constant of $2.1 \times 10^8\ M^{-1}\ s^{-1}$. The fact indicates considerable triplet energy transfer of **3c** to **1c** in DCE. In MTHF, however, no energy transfer was detected, which is consistent with no triplet sensitization of **3c** in the rearrangement of **1c** in this solvent as mentioned in the last section. It is because the triplet energy level of **3c** in MTHF may be stabilized greater than that of **1c**. Therefore, **3c** formation in the irradiation of the MTHF solution of **1c** may be attributable to an intersystem crossing.

Figure 6 conclusively shows reaction scheme and energy diagram of the photorearrangement reaction of arene oxides reported here. Photoexcitation of these oxides leads to the formation of the lowest singlet excited state S_1 followed by the corresponding oxepin formation (the reaction quantum yields in **1a** and **1c** are 0.4 and 0.2, respectively). Intersystem crossing from S_1 to T_1 is predominant in **1b** and appreciable in **1c**, while negligible in **1a**. Photoexcitation of phenols **3a** and **3c** added to the DCE solution of **1a** and **1c** leads to the triplet energy transfer; **3a**→**1a** and **3c**→**1c**. The rearrangement reaction of arene oxides to phenols occurs via the triplet state. However, no triplet energy transfer occurs in such a polar solvent as MTHF and/or acetonitrile because of stabilization of T_1 energy of phenol greater than that of the parent oxide. The reaction mechanism proposed here is well consistent with the results of product analysis reported in the several literatures.[1–4]

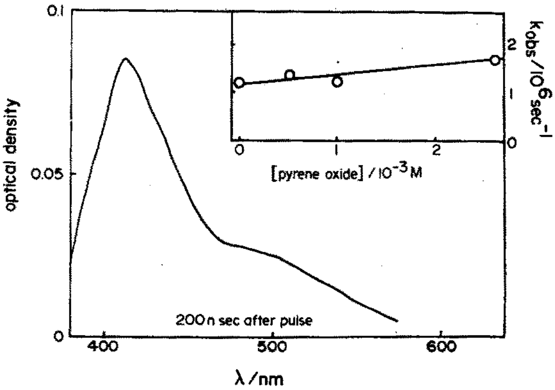


Fig. 5. T–T absorption spectrum at 200 nsec after a laser pulse for an aerated DCE solution of **3c** (4.1×10^{-3} M). An inset shows the plots of apparent decay rate constant of the T–T absorption against the concentration of **1c** added.

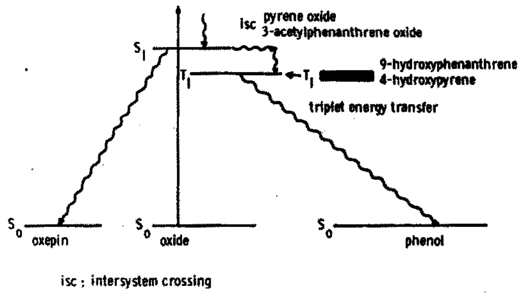


Fig. 6. Diagramatic reaction scheme for the photorearrangement reaction of arene oxides (**1a**–**1c**).

EXPERIMENTAL

Materials. Arene oxides were prepared according to known procedures. Dialdehydes obtained by ozonolysis of phenanthrene and 3-acetylphenanthrene were cyclized by hexamethyl phosphorous triamide and purified by chromatography on an alumina column. All compounds used in this paper were identified by IR, NMR, UV and elementary analysis.

9,10-Epoxy-9,10-dihydrophenanthrene (**1a**), m.p. 100–102°; IR (KBr) 3000 (methine group), 890 (oxirane) cm^{-1}; (Found: C, 86.76; H, 5.02. Calc. for $C_{14}H_{10}O$: C, 86.57; H, 5.10%).

3-Acetyl-9,10-epoxy-9,10-dihydrophenanthrene (**1b**), m.p. 144–148° recrystallized from benzene. IR (KBr) 3000, 1665 (CO), 880 cm^{-1}; (Found: C, 80.72; H, 4.99. Calc. for $C_{16}H_{12}O_2$: C, 81.34; H, 5.12%).

4,5-Epoxy-4,5-dihydropyrene (**1c**) was obtained from cyclization of 4,5-trans-dihydro-4,5-dihydroxypyrene by sulfuran reagent reported in the previous paper,[8] recrystallized from benzene–hexane, m.p. 140–160 (decomp); IR (KBr) 3000, 880 cm^{-1}; (Found: C, 88.13; H, 4.72. Calc. for $C_{16}H_{10}O$: C, 88.05; H, 4.62%).

9-Hydroxyphenanthrene (**3a**) was obtained by hydrolysis of 9-methoxyphenanthrene which was prepared by heating 9-bromophenanthrene with NaOMe/CuI, recrystallized from benzene, m.p. 152–155°; (Found: C, 86.59; H, 5.04. Calc. for $C_{14}H_{10}O$: C, 86.57; H, 5.19%). BF_3-etherate catalysed rearrangement of **1a** also gave pure 9-hydroxyphenanthrene.

3-Acetyl-9-hydroxyphenanthrene (**3b**) was prepared by photolysis of **1b** in deaerated benzene soln, and purified by preparative tlc (silica; benzene–CH_2Cl_2). The crystals obtained were recrystallized from CH_2Cl_2–hexane, m.p. 197.5–198.5°; (Found: C, 81.52; H, 5.23. Calc. for $C_{16}H_{12}O_2$: C, 81.34; H, 5.12%).

4-Hydroxypyrene (**3c**) was obtained by hydrolysis of **1c** in aqueous HCl (pH 1) at 50°, purified by column chromatography and recrystallized from MeOH–benzene, m.p. 202°; IR (KBr) 3300, 1220 cm^{-1}; (Found: C, 88.05; H, 4.62. Calc. for $C_{16}H_{10}O$: C, 87.73; H, 4.70%).

Dibenz[b,d]*oxepin* (**2a**). An aerated CH_2Cl_2 soln of **1a** was irradiated at low pressure mercury lamp (1 KW). The solvent was evaporated and residue was chromatographed on silica gel and recrystallized from MeOH, m.p. 47°; the compound was identified by NMR and UV.[1]

Tribenz[b,c,d]*oxepin* (**2c**). A soln of **1c** (22 mg) in acetonitrile was irradiated by low pressure mercury lamp for 1 hr. Though some pyrene still remained, the soln was dried and the residue was chromatographed on silica gel. The major fraction was crystallized from MeOH, m.p. 134°; (Found: C, 87.68; H, 4.98. Calc. for $C_{16}H_{10}O$: C, 88.05; H, 4.62%).

Steady-state irradiation and transient spectroscopy. Steady light from a Xe arc grating monochromater unit (JASCO-CRM-100) was employed in the steady-state photolysis. Electronic absorption spectra were measured on a Hitachi 323 spectrophotometer. Fluorescence and phosphorescence were measured on a Hitachi MPF-4 spectrophotometer. Good commercial solvents (Dotite Spectrosols) were used, and 2-methyltetrahydrofuran was purified by refluxing with K metal and by distillation. The sample solns were contained in a rectangular quartz cell (1 cm) equipped with graded seals and degassed by freeze-thaw cycles if necessary.

Quantum yield of oxepin formation was evaluated from the number of oxepin molecules formed and that of the absorbed photons per unit time. The former was estimated from the net increase of the optical density due to oxepin and the molar extinction coefficient. The latter was obtained by the modified ferrioxalate actinometry described previously.[9] In order to reduce the inner filter effect of oxepin, the actinometry was performed at the early stage of the reaction.

The experimental set-up for the transient absorption is the same as that described in previous papers[10] by Yoshihara *et al.* The coaxial nitrogen gas laser was used as an exciting light source. The pulsed analytic Xe lamp (EG&G, FX 124) of a few microsecond duration was synchronized with an actinic laser pulse. Both laser and Xe light were focussed through an aperture onto the sample cell (2 mm) with common lenses.

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[5] The Ketelaar plot for this interaction gives a good linear line corresponding an equilibrium constant of 51 M^{-1}.
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[7] Since these oxides (**1b** and **1c**) are slightly photo-excited, the data of the quenching rate constant obtained in the condition of high quencher concentration are somewhat unreliable.
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