

a 400-MHz ¹H NMR spectrum of the aromatic H atoms of compound 7: while a spectrum of a linear (2,3) connected product should show two triplet, two doublet, and two singlet signals, the obtained spectrum exhibited two triplet signals at 7.30 and 7.46 ppm and four doublet signals at 7.23, 7.68, 7.81, and 7.93 ppm which are in agreement with the angular (1,2) connection (meta and para couplings can be neglected here because of very small coupling constants). Also, the photocyclization of analogous naphthyl vinyl sulfides leads only to 1,2-fusion products.⁵

Further photoproducts were obtained when nitrogen-flushed *n*-hexane or MCH was used as solvent. On irradiation of 2 in these solvents, not only 7 was detected (by its NMR absorption at 4.3 ppm) but also an additional NMR signal appeared at 5.8 ppm, indicating that the *trans* isomer of 7 was also produced as expected from Schultz's results. *Cis* and *trans* isomers occurred in the ratio of 30:70. On the other hand, irradiation of 4 leads only to the NMR spectrum of 9 just as in the acetic acid containing solvent mixture since the *cis* and *trans* isomers are equivalent in this case. Irradiations of 3 and 5a,b yielded mainly polymer materials and only small amounts of the cyclization products. Photopolymerization of 3 occurred also when a triplet sensitizer (propiophenone) was excited in the presence of 3, indicating that polymerization proceeds via the triplet state.

When air-saturated solutions of 3, 4, and 5a in *n*-hexane were irradiated, compounds were formed with molecular weights exceeding those of the educts by 32 mass units, i.e., the mass of O₂ (or two O atoms). The O₂ adduct isolated after irradiation of 3 showed infrared absorption bands at 1685, 1735, 1755, and 1775 cm⁻¹ which were not present in the spectrum of the educt. These absorptions are typical for compounds containing ozonide structural elements.⁶ However, irradiations of the aryloxy enones 1 and 2 under the same conditions lead to the addition of only one oxygen atom, as seen by the only 16 mass units higher molecular mass. No IR bands typical for ozonide absorptions were observed.

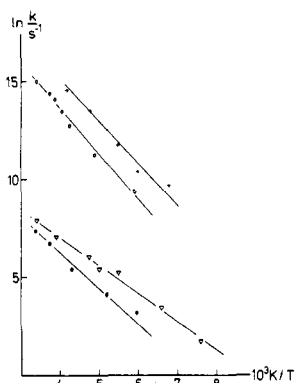
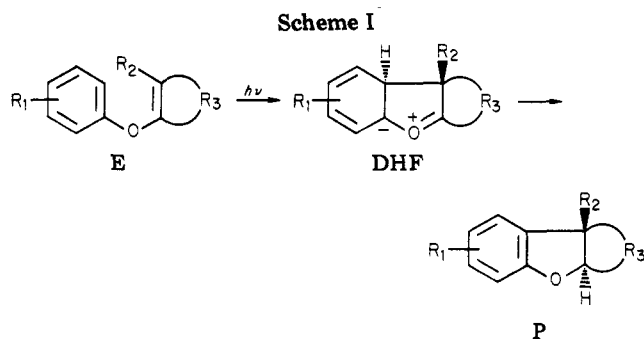


Figure 1. Arrhenius diagrams of triplet decay of 2 (O) and 3 (+) and of DHF decay of 13 (▽) and 14 (●) all in degassed MCH solutions.

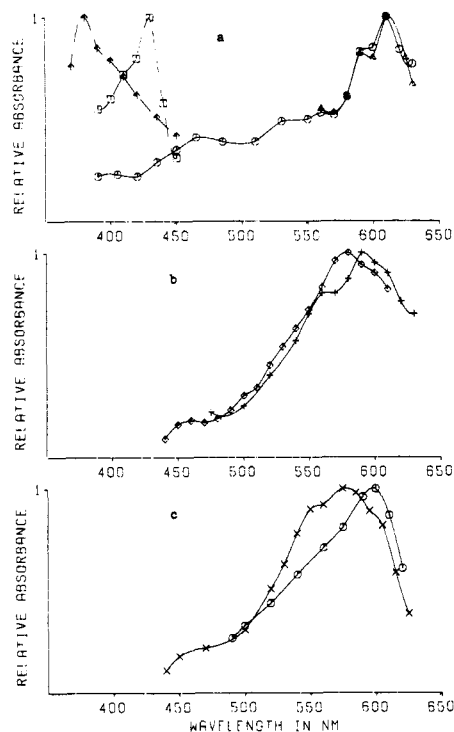


Figure 2. Transient absorption spectra of degassed solutions of aryl vinyl ethers in MCH after flash excitation: a, DHF absorption of 11 (Δ) and 12 (O) together with T₁ → T_n absorption of 1 (upward arrow) and 2 (□); b, DHF absorption of 13 (+) and 14 (diamond); c, DHF absorption of 15a (x) and 15b (O).

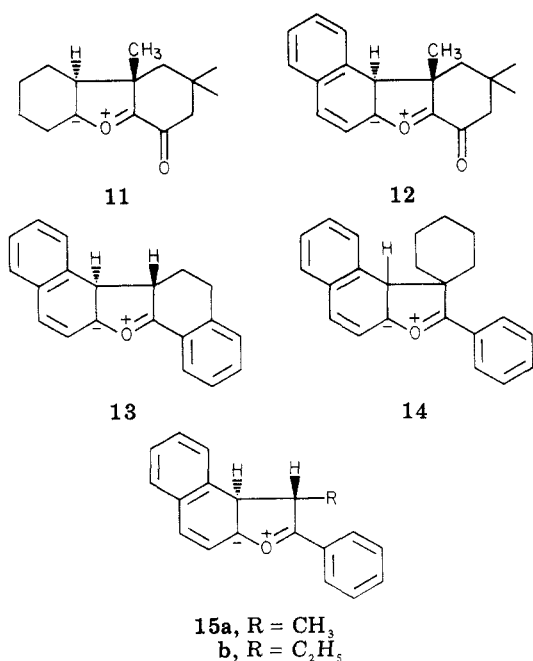
Flash Experiments. (1) Microsecond Region. After flashing ca. 5 × 10⁻⁵ M degassed solutions of 1–5 in MCH by a conventional flash apparatus one observes colored transients which disappear following first-order kinetics with lifetimes τ ranging between 4 × 10⁻⁴ and 9 × 10⁻⁴ s at room temperature. Activation energies of 10 and 16

(5) Schultz, A. G.; DeTar, M. B. *J. Am. Chem. Soc.* 1976, 98, 3564–3572.

(6) (a) Susz, B.; Dallwigk, E.; Briner, E. *Helv. Chim. Acta* 1952, 35, 345–353. (b) Dalwigk, E.; Susz, B.; Briner, E. *Ibid.* 353–362.

kJ/mol, respectively, were determined for the anaerobic decay of the transients obtained from **3** and **4** (see Figure 1). Comparatively low frequency factors of 3×10^5 and $9 \times 10^5 \text{ s}^{-1}$, respectively, were calculated from the data. In air-saturated solutions ($[\text{O}_2] = 2 \times 10^{-3} \text{ M}$) the decay constants $k = k_q[\text{O}_2] + 1/\tau$ are higher by a factor of 18 in the case of **5b** and by a factor of 15 when **4** was flashed. The bimolecular rate constant k_q of the reaction of a transient with oxygen was calculated from k and $1/\tau$ and gave values of less than $10^8 \text{ M}^{-1} \text{ s}^{-1}$, i.e., well below the limit set by diffusion control. Surprisingly, the lifetime of the transient obtained upon flashing a solution of **2** was unaffected by the presence of oxygen. However, a difference in reactivity against oxygen between **2** on the one hand and **4** and **5b** on the other was already indicated by the steady-irradiation experiments. At any rate, the transients were shown to be ground-state intermediates because of their comparatively long lifetimes and the fact that no diffusion-controlled oxygen quenching rates were found.

By extrapolation of decay curves to zero time at different wavelengths, absorption spectra of the transients were obtained (see Figure 2). The spectra show absorption maxima between 575 and 610 nm; i.e., they are located in the same wavelength region as those of the zwitterionic intermediates occurring in the photocyclization of the analogous *S*-aryl vinyl sulfides.^{4,5} Kinetic as well as spectral evidence, therefore, suggests that zwitterionic resonance structures like **11**–**15** should be assigned to the transients observed here.



In air- and oxygen-saturated solutions, the quantum yield of **12** dropped to ca. 60% and 15%, respectively, of its value obtained in degassed solutions (the optical density at the wavelength of the absorption maximum was taken as a measure for relative quantum yield). These observations suggest a triplet precursor of **12** which is quenched by oxygen at a rate proportional to the oxygen concentration. On the other hand, the quantum yield of **14** dropped only to 95% in aerated solution. Obviously, oxygen quenching is less efficient in this case. A likely cause for this is the occurrence of a very fast *cis*–*trans* isomerization about the olefinic double bond in the supposed precursing triplet state. Such *cis*–*trans* isomerizations are not possible for compounds like **1**–**3** in which the double

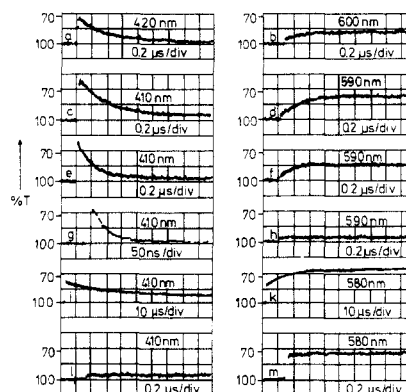


Figure 3. Oscilloscope traces of transient absorptions after laser flash excitation: a and b, **1** in degassed MCH; c and d, **2** in degassed MCH; e and f, **2** in air-saturated MCH; g and h, **2** in oxygen-saturated MCH; i and k, **3** in degassed MCH; l and m, **5a** in degassed MCH (a–h, l, and m at 23 °C, i and k at –117 °C).

bond is incorporated in a ring system. Rapid *cis*–*trans* isomerizations of olefinic double bonds competing with ring closure have been established to occur also in the triplet states of the analogous aromatic enamines.^{3,7} Also, effects as described above were observed in a study on the photocyclization of aryl vinyl sulfides⁴ and were explained analogously. Further evidence for the occurrence of a triplet side reaction is the fact that the quantum yields of **14**, **15a**, and **15b** decrease when the temperature is lowered. For example, the quantum yield of **15b** at –101 °C is only 15% of that at room temperature, indicating that the *cis*–*trans* isomerization requires a lower activation energy than the ring-closure reaction. No decrease of quantum yields was observed for the zwitterions of cyclic vinyl ethers **11**–**13** between room temperature and about –160 °C. Below this temperature the quantum yield of **13** fell rapidly, and at about –170 °C phosphorescence of the probe became detectable, indicating that now the triplet state of **3** is depleted mainly by emission which is faster at this temperature than the formation of **13**.

The anaerobic decay of the zwitterions **11**–**15**, i.e., the 1,4 hydrogen shift $\text{DHF} \rightarrow \text{P}$ in Scheme I, was found by Schultz et al.^{1b} to be a unimolecular step in aprotic solvents and a partly bimolecular one in protic solvents. This was concluded by the authors from irradiation experiments in methanol-*d* where deuterium was found in the irradiation products. Consequently, a decrease of the lifetimes of the zwitterionic DHF intermediates is expected whenever a protic solvent is used instead of the aprotic MCH. Flash experiments with **1** and **2** in methanol do, in fact, confirm this expectation since no DHF absorption was observed when a conventional flash apparatus was used. However, the lifetime of **14** (0.63 ms at room temperature in MCH) was not reduced in degassed methanol, so that a generalization of the above consideration is not warranted. Further irradiation experiments with **4** in protic solvents are necessary to clear this point.

(2) Nanosecond Region. In order to study the formation of DHF and to find direct evidence for its triplet precursor, flash experiments on a submicrosecond time scale were carried out. For this purpose degassed solutions of **1**–**3** in MCH were subjected to the 308-nm emission of an excimer laser. Typical records of the change in transmission after laser flash excitation are reproduced in Figure 3. The absorption of two different transients was observed in each of these experiments. One of them ab-

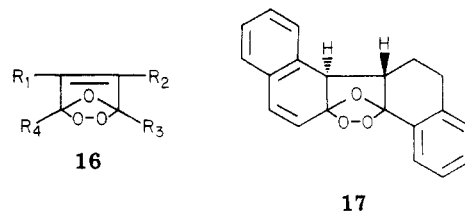
ternative ways: either the excited triplet state of DHF is indeed not an intermediate in this reaction sequence or its decay is faster than that of $^3E^*$ under all conditions investigated. In this regard, the photocyclization of aryl vinyl ethers shows a very close analogy to that of aryl vinyl sulfides while for the photocyclization of aromatic enamines an adiabatic mechanism has been verified. The possibility that the triplet-state absorption observed in the laser-flash experiments belongs to the triplet state of DHF instead of $^3E^*$ is remote since in that case the quantum yield of the triplet absorption should decrease in oxygen-containing solutions by the same amount as that of the DHF absorption. This is definitely not the case (compare Figure 3c,d with Figure 3e-h).

Zwitterions analogous to DHF which appear as intermediates in the photocyclizations of *N*-aryl enamines and also of diphenylamines have been shown to undergo thermal ring-opening reactions leading back to the educts.^{7,8} This was concluded from the Arrhenius diagrams of the anaerobic zwitterion decay in which two distinct decay channels differing in activation energy were shown to exist. The conclusion was also tested by quantum yield measurements. No evidence for the appearance of such a ring-opening reaction which would have diminished the ring-closure quantum yield was found for DHF in the present study. Hereby, again, the ethers differ from the amines and behave more like the analogous aryl vinyl sulfides.^{4,7,8} However, since measurements of the dependence on temperature of the ring-closure quantum yields for the ethers as well as for the sulfides have not yet been performed, the possibility of detection of a ring-opening step of DHF with an activation energy similar to that of the hydrogen-shift reaction (k_3) is not ruled out. Extraordinary frequency factors for the anaerobic zwitterion decay are not uncommon in these systems.^{7,8}

The photopolymerization of aryl vinyl ethers occurring under some conditions seems to follow a completely different route compared with that of the photopolymerization of analogous sulfides. In the latter case, polymerization has been shown to be initiated by C-S bond cleavage after excitation to higher singlet levels competing with internal conversion and intersystem crossing to the triplet state from which the ring-closure reaction starts.⁹ Therefore, triplet decay and subsequent formation of zwitterions was only detected after laser-flash excitation to low-lying singlet states. Whenever the sulfides had been excited to higher levels, completely different features appeared in the oscilloscope traces. Since analogous features were not observed in the present study, it seems reasonable to assume that here polymerization is caused by reirradiation of already cyclized products. This assumption is strongly supported by the observation that polymerization also occurs upon photosensitization by propiophenone.

The photochemical addition of oxygen seems to be a peculiarity of the photochemistry of aryl vinyl ethers. In the case of analogous sulfides, no reaction of the intermediate zwitterions with oxygen is known⁴ while *N*-methyl-4a,4b-dihydrocarbazole, the zwitterionic intermediate of the photocyclization of *N*-methyldiphenylamine, reacts with oxygen to yield H₂O₂ and *N*-methylcarbazole.⁸ The ethers 3-5 were shown to react with oxygen in the state of the intermediates 13-15 since their decay constants were enhanced drastically. Singlet oxygen produced by quenching of the triplet states of the ethers may be involved in the oxygen addition reaction since the addition

of singlet oxygen to compounds containing diene or polyene structural elements like DHF is well-known.¹⁰ Also, the photosensitized autoxidation of several furans¹¹ has been considered to proceed via O₂ adducts containing ozonide structures like 16. Since the O₂ adduct isolated



after irradiation of 3 in air-saturated MCH showed IR absorption bands typical for ozonide structures, the formation of 17 seems to be probable. Hereby a reaction capable of trapping DHF intermediates is possibly found. Less clear are the cases of 1 and 2 where the lifetime of the zwitterion was unaffected by the presence of oxygen and where only one oxygen atom was found to have been incorporated. Further investigations are necessary to decide whether the educt, an intermediate, or the product reacts with oxygen.

Conclusions

For the practical application of the photocyclization of aryl vinyl ethers, the results suggest use of oxygen-free solutions since oxygen reacts with the intermediate zwitterions to yield byproducts and since it reduces the quantum yield by quenching the triplet states of the ethers. Also, other triplet quenchers should be excluded. Careful selection of the solvent is required in order to suppress polymer formation and to avoid production of mixtures of stereoisomers due to hydrogen exchange in protic solvents. Lowering the temperature will favor *cis-trans* isomerization about the olefinic double bond and will thereby diminish the cyclization quantum yield unless the double bond of the aryl vinyl ether is incorporated in a ring system. Therefore, a mixture of *cis-trans*-isomerized products will be formed whenever reirradiation of isomerized educts can take place.

Experimental Section

Preparation of Aryl Vinyl Ethers. 2-Phenoxy-3,5,5-trimethyl-2-cyclohexen-1-one (1) was prepared as described by Schultz et al.^{1b} and showed the physical and spectroscopic properties reported there.

2-(Naphth-2-yloxy)-3,5,5-trimethyl-2-cyclohexen-1-one (2) was prepared in an analogous manner: yield 73%; mp 120 °C; ¹H NMR (CDCl₃) 1.1 (6 H, s), 1.9 (3 H, s), 2.4 (4 H, s), 7.0-7.9 ppm (7 H, m).

The preparation of 1-(naphth-2-yloxy)-3,4-dihydronaphthalene (3), (naphth-2-yloxy)cyclohexylidenebenzylmethane (4), 1-(naphth-2-yloxy)-1-phenyl-2-methylethene (5a), and 1-(naphth-2-yloxy)-1-phenyl-2-ethylethene (5b) has been published elsewhere.¹²

Flash Experiments. Details of the millisecond and nanosecond flash apparatuses have been published elsewhere.⁹ Most of the experiments were carried out in methylcyclohexane (MCH) solutions containing 3% of 2-methylbutane. The purification of MCH and degassing and drying procedures have been described elsewhere.⁴ Some experiments were carried out in methanol solution (Merck, Uvasol) which was used without further puri-

(8) Förster, E. W.; Grellmann, K. H.; Linschitz, H. *J. Am. Chem. Soc.* 1972, 95, 3108-3115.

(9) Wolff, T. *J. Photochem.* 1979, 11, 215-217.

(10) Gollnick, K. In "Singlet Oxygen. Reactions with Organic Compounds and Polymers"; Ranby, B.; Rabek, J. F., Eds.; Wiley: Chichester-New York-Brisbane-Toronto, 1978; pp 111-134.

(11) Schenck, G. O. *Justus Liebigs Ann. Chem.* 1953, 584, 156-176.

(12) Wolff, T.; Reiffenrath, V. *Synthesis* 1980, 847-849.

fication. The concentration of aryl vinyl ethers was about 5×10^{-5} M. For low-temperature experiments the cooling technique of Fischer¹³ was applied.

Steady Irradiations. Solutions (5×10^{-3} M) of aryl vinyl ethers in MCH, *n*-hexane, or methanol/acetic acid/benzene (1:1:1) were irradiated in an apparatus described elsewhere.⁷ The irradiations were continued until constancy of the UV spectra indicated the end of the reaction. Then the solvents were evaporated and the products analyzed by ¹H NMR, mass, and IR spectroscopy.

Instruments: Beckman Acta M VII UV-spectrophotometer, Varian EM 360 A (60 MHz) and Bruker-Spectrospin WH-400

(400 MHz) NMR spectrometers, Varian MAT 112 mass spectrometer.

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Registry No. 1, 55488-88-5; 2, 75975-15-4; 3, 611-49-4; 4, 75975-16-5; 5a, 75975-17-6; 5b, 75975-18-7; 7, 75975-19-8; 7 (trans isomer), 75975-20-1; 8, 75975-21-2; 9, 75975-22-3; 10a, 75975-23-4; 10b, 75975-24-5; 11, 75975-25-6; 12, 75975-26-7; 13, 75975-27-8; 14, 75975-28-9; 15a, 76024-68-5; 15b, 75975-29-0.

(13) Fischer, E. *Mol. Photochem.* 1970, 2, 99-102.

Keto Oxetanes Produced from Photocycloaddition of *o*-Quinone and Their Thermolysis. Reaction of 9,10-Phenanthrenequinone with Internally Highly Strained Cyclic Olefins

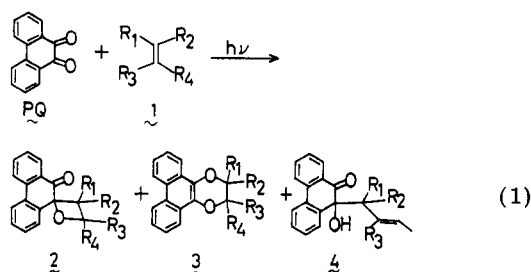
Kazuhiro Maruyama,* Masami Muraoka, and Yoshinori Naruta

Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606, Japan

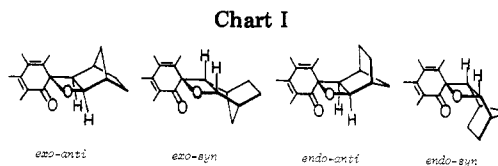
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The photocycloaddition reaction of 9,10-phenanthrenequinone (PQ) with alicyclic (1a-e) and bicyclic olefins (1f-1) was examined upon irradiation with visible light (>420 nm). Alicyclic olefins gave three kinds of products, keto oxetanes (2), dihydrodioxines (3), and 4, while bicyclic olefins exclusively gave keto oxetanes in fair to high yields (21-90%). These marked differences were elucidated in terms of the *s* character of intermediary biradicals. Thermolysis of the five keto oxetanes obtained (2a,d,g,i,l) was examined in basic media and occurred in two different fashions (paths A and B in Scheme I). Correlation between the bond strength of the oxetane ring and the structure of intermediary biradicals is discussed.

The photocycloaddition reaction of 9,10-phenanthrenequinone (PQ) with olefins gives mainly two types of products, keto oxetane 2 ($[2_{\pi} + 2_{\pi}]$ addition) and dihydrodioxine 3 ($[4_{\pi} + 2_{\pi}]$ addition; eq 1). The relative



yield of the two products (2 and 3), however, is strongly dependent on the structure of olefins. The true reason which governs the relative product ratio still remains to be clarified. In addition, α -hydrogen abstraction product 4 is often found. The reaction has been intensively investigated in a limited number of 1,2-quinones.¹ The lack of systematic investigation is partly due to (1) the photostability of keto oxetanes, which easily rearranged and decomposed under irradiation of UV light,^{2,3} and (2) the



difference of the irradiation conditions.

In a previous paper,³ we reported the products and the reaction pathway in the photochemical reaction of alicyclic olefins and PQ. Bicyclo[2.2.1]hept-2-ene, compared with other alicyclic olefins, gave the corresponding keto oxetane in a high yield with a high selectivity, whereas *cis*- and *trans*-stilbene gave solely the corresponding dihydrodioxine of the same stereochemistry. The outstanding difference is suggestive for seeking the true factors governing the relative product ratio. In this paper, we will describe (1) the correlation between the selectivity (2 vs. 3) and the ring size of the olefin in the photochemical reaction with PQ and (2) the fate of the intermediary biradicals generated by thermolysis of 2.

Results

Photochemical Reaction of PQ with Cyclic Olefins. In order to avoid the successive photochemical reactions of keto oxetanes, we irradiated a benzene solution of PQ

(1) For reviews of photochemical reactions of quinones, see: (a) Pfundt, G.; Schenck, G. O. In "1,4-Cycloaddition"; Hamer, J., Ed.; Academic Press: New York, 1967, pp 345-417; (b) Bruce, J. M. *Q. Rev., Chem. Soc.* 1967, 21, 405; (c) Bruce, J. M. In "The Chemistry of Quinonoid Compounds"; Patai, S., Ed.; Wiley: New York, 1973, Part 1; pp 345-538.

(2) Farid, S.; Scholz, K.-H. *Chem. Commun.* 1969, 572.

(3) Maruyama, K.; Iwai, T.; Naruta, Y.; Otsuki, T.; Miyagi, Y. *Bull. Chem. Soc. Jpn.* 1978, 51, 2052.