Flash Photolytic Studies on the Photoconversion of Aryl Vinyl Ethers to Dihydrofurans

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The reaction mechanism of the photocyclization of aryl vinyl ethers was derived from results obtained by means of flash photolysis in the millisecond and submicrosecond time ranges and of steady-irradiation experiments. Decay times, absorption spectra, and quantum yields of intermediates were measured. The reaction proceeds via the excited triplet state of the educts and zwitterionic ground-state intermediates which rearrange by mono-
or bimolecular 1,4 hydrogen shifts to yield the products. Some zwitterions also undergo oxygen addition react Several cyclized products polymerize upon reirradiation. The overall reaction is shown to be distinct but partly analogous to the photocyclization of aryl vinyl sulfides and aromatic enamines.

The photocyclization of aryl vinyl ethers has recently been established as a key step in the preparation of dihydrofuran derivatives¹ ($\check{E} \rightarrow \check{P}$, Scheme I), i.e., substances of considerable pharmaceutical interest. For instance, the photocyclization of 2-aryloxy enones was used successfully in the total synthesis of dl -lycoramine,^{1a} a morphine alkaloid. Very good chemical yields (up to 90%) were reported,^{1b} and comparatively concentrated solutions (ca. 0.02 M) can be irradiated.

However, few mechanistic details of this reaction were reported so far. Schultz et al.^{1b} have mentioned a sensitization experiment indicating triplet intermediates. They also assumed a zwitterionic ground-state intermediate (DHF in Scheme I) but did not present experimental evidence for its appearance. Further information was obtained with respect to the second step $(DHF \rightarrow P)$ in Scheme I: in aprotic solvents the trans-fused dihydrofuran P was obtained predominantly while the less strained cis-fused stereoisomer of P was obtained exclusively in acidic solvents. Intermediate behavior was observed in protic solvents. Since irradiation in deuterated protic solvents led only to labeling of the cis-fused isomer, it was concluded that a bimolecular reaction step competes with a unimolecular 1,4 hydrogen shift in the net reaction DHF \rightarrow P.

From a theoretical point of view it should be interesting to know whether an adiabatic mechanism² is operating in the reaction sequence, since previous mechanistic investigations of N -aryl enamines³ and S -aryl vinyl sulfides⁴ had shown that they differ: an adiabatic mechanism was verified only in the former system. Therefore, in the present work steady-irradiation experiments and flash photolyses were carried out in order to elucidate the mechanism of the photocyclization of aryl vinyl ethers. Compounds 1-5 were chosen for this investigation. Of these, only 1 has been studied previously. Schultz and Luccile had shown that the photocyclization of 1 yielded **6.** Therefore, a brief examination of the photoreactions of **2-5** was necessary before flash experiments were per-

formed in order to prove the occurrence of photocyclizations. Since the solvents used by Schultz et al.' (methanol, acetic acid, benzene, and mixtures of these) are not suitable for flash experiments (especially not at low temperatures), further experiments were necessary with saturated hydrocarbon solvents like n-hexane or methylcyclohexane (MCH).

Results

Steady Irradiation Experiments. In nitrogen-purged M solutions **of 2-5** in methanol/acetic acid/benzene **(1:l:l)** products 7-10 were formed on Pyrex-filtered irradiation. These products were identified by the characteristic NMR signals of the hydrogen atoms attached to the bridge carbon atoms neighboring the ether bond showing chemical shifts similar to those reported by Schultz et al.^{1b} for 6 (4.5 ppm) and related compounds **(4.5-5.8** ppm). Corresponding **lH** *NMR* signals were found at **4.3** ppm for compound 7, at **5.8** ppm (doublet) for **8,** at **5.6** ppm for **9,** and at **5.4** ppm (doublet) for **10a** and 10b (measured in CDCl₃ vs. $Me₄Si$). Moreover, the mass spectra of the products show the same molecular weights **as** the educts but different fragmentation patterns, which is consistent with assignment of the products structures $7 - 10.$

Direct information concerning the way in which the dihydrofuran and the naphthalene ring systems are connected in the cyclization products 7-10 was obtained from

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a 400-MHz 'H 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 nitrogenflushed 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 O_2 (or two O atoms). The O_2 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** *(0)* **and 3** (+) and of DHF decay of $13 \times v$ and $14 \times v$ 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 $T_1 \rightarrow T_n$ absorption of 1 **(upward arrow) and 2** *(0);* **b,** DHF **absorption of 13** (+) **and 14 (diamond); c,** DHF **absorption of 15a** *(X)* **and 15b** *(0).*

Flash Experiments. (1) Microsecond **Region.** After flashing ca. 5×10^{-6} 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**

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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 9×10^5 s⁻¹, respectively, were calculated from the data. In air-saturated solutions ($[O_2] = 2 \times 10^{-3}$ M) the decay constants $k = k_q[O_2] + 1/\tau$ 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 $10^8 \,\mathrm{M}^{-1} \,\mathrm{s}^{-1}$, 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; Le., 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; 1 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 $15\overline{b}$ 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, confim 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-

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sorbing mainly around 600 nm is being built up during the observation time. By measurement of the optical density **as** a function of wavelength at **1.8** *ps* after excitation, i.e., at the end of the oscilloscope traces in Figure 3, absorption spectra were obtained which coincide with the "zero time" spectra of the zwitterionic DHF intermediates in the conventional experiments shown in Figure **2.** Also, the temperature dependence of the yields of these transients agrees with that observed for the DHFs. Therefore, these gradually emerging transients are identified as the DHF intermediates **11-13.**

At shorter wavelengths, around 410 nm, shorter lived transients were observed which decay (within experimental error) at the same rate as the DHF absorption rises. Thereby, in all probability, the decaying transients are shown to be the precursors of the DHFs. The steplike increase "immediately" after flash excitation observed in the longer wavelength region (Figure 3b,d,f,h,k) is due to overlapping absorptions of the precursing and succeeding transients **as** can be shown under conditions where no DHF absorption is observed (see below and Figure 4). In order to confirm the supposed triplet character of the precursors, quenching experiments with oxygen were performed, using aerated and oxygen-saturated solutions of 2. The rate constants of the decay at 410 nm were k_0 $= 1.9 \times 10^6$ s⁻¹ in degassed, $k = 4.34 \times 10^6$ s⁻¹ in air-saturated, and $k = 1.9 \times 10^7$ s⁻¹ in oxygen-saturated solutions. From eq 1 the quenching constants (k_a) can be determined.

$$
k = k_0 + k_q[O_2] \tag{1}
$$

With $[O_2] = 2 \times 10^{-3}$ and 10^{-2} M in air- and oxygen-saturated methylcyclohexane, k_a is found to be 1.2×10^9 and 1.7×10^9 M⁻¹ s⁻¹, respectively. By the quenching reaction, of course, the quantum yield of **12** is lowered. Taking the values for the absorbance A at 590 nm in degassed $(A_0 =$ 0.112), aerated $(A = 0.062)$, and oxygen-saturated $(A = 0.062)$ **0.015)** solutions as measures for relative quantum yields (Figure 3d,f,h; "plateau region"), an independent check on the value of k_a can be made by using eq 2. Values of 7.7

$$
A_0/A = \phi_0/\phi = 1 + k_q(1/k_0)[\mathcal{O}_2]
$$
 (2)

 \times 10⁸ M⁻¹ s⁻¹ for the air-saturated and of 1.2 \times 10⁹ M⁻¹ s⁻¹ for the oxygen-saturated solutions were calculated in this way. These numbers are still within the accuracy limits of the determination (flash intensities vary within **10%).** Moreover, the values agree well with those reported for oxygen quenching of the triplet state of analogous aryl vinyl sulfides.⁴

By extrapolation of the triplet decay curves to zero time at different wavelengths, $T_1 \rightarrow T_n$ absorption spectra can be obtained. This was carried out for the triplet states of **1** and **2.** The spectra are shown in Figure **2.** Activation energies for the triplet decay in degassed solution, i.e., for the ring-closure reaction, were determined for **2** and **3 as** 19 and **17** kJ/mol, respectively (see Figure **1).** These values, of course, pertain to the temperature dependence of the rate constants of the corresponding increase of DHF absorptions.

It should be kept in mind that the production of DHF from the excited triplet state of the ether is observed in the case of **3** (Figure 3i,k) **as** well **as** in the other *casea* while steady irradiation under the same conditions leads to polymer formation (see above). This indicates that the polymerization may be a two-photon process whereby the cyclized products are reirradiated and undergo photopolymerization.

The decay of the triplet states of the acyclic ethers **4, 5a,** and **5b** could not be resolved within the time resolution

410n _m	580 _{nm}
70 10	70 100
0 us/div %T	20 us/div
70 410 nm 100	70 590nm 10C

Figure 4. Oscilloscope traces of transient absorptions after laser **flash excitation: a and b, 3 in degassed MCH at -170 "C; c and** d, 2 in degassed methanol at 23 °C.

of the apparatus used. Therefore the DHF absorption is seen to be formed "immediately" after flash excitation (Figure 31,m). This observation confirms the assumption of a fast, rate determining cis-trans isomerization in the triplet state which was derived from the quenching experiments discussed above.

Finally, evidence for a triplet mechanism was obtained from two sensitization experiments: degassed solutions containing 10^{-2} M propiophenone and 10^{-3} M 2 or 5a, respectively, were subjected to the 350-nm emission of an excimer laser. Under these conditions only the propiophenone was excited. Hereby the absorptions of **12** and **15a** were observed, which is only possible when triplettriplet energy transfer from propiophenone to the ethers and subsequent ring closure occurs. The quantum yield of **12** was higher than that of **15a** by a factor of about 35, provided the extinction coefficients of the zwitterions **as** well **as** the quenching efficiencies of the ethers are similar, which **seems** reasonable. **Again,** this effect is a consequence of the fast cis-trans isomerization of **5a** in the triplet state which diminishes the ring-closure quantum yield.

Two different conditions were found under which no absorption attributable to DHF intermediates could be obtained. In one experiment a degassed solution of **3** in MCH was cooled to **-170** "C. At this temperature the ring-closure reaction is hindered by activation energy, and other deactivation routes of the triplet state (phosphorescence, etc.) prevail (see Figure 4a,b). In the other experiment, a degassed solution of **2** in methanol was flashed. Under these conditions bimolecular decay of **12** dominates **as** mentioned above. Since no absorption of **12** is observed (Figure 4d) while the ring closure clearly takes place in protic solvents (see steady-irradiation experiments and ref **l),** the bimolecular decay, i.e., the reaction with the solvent, must proceed faster than the decay of the triplet state of **2** so that no measurable amount of **12** is formed. Both experiments confirm that the steplike increase observed in Figure 3b,d,f,h,k belongs to the triplet absorption since the decay rate at 590 nm agrees with that at 410 nm (see Figure 4).

Discussion

Summarizing the results the reaction sequence shown in Scheme I1 is established. Therein **lE*** and *3E** represent the first excited singlet and triplet states of aryl vinyl ethers **E**. k_i is the rate constant of reaction step i (=1-4), k_{α} is that of the quenching reactions, and k_{α} is that of the cis-trans isomerization about the olefinic double bond. "Trivial" deactivation routes of the excited states (fluorescence, etc.) have been omitted in order to simplify Scheme 11.

The fact that no adiabatic reaction step ${}^{3}E^{*} \rightarrow {}^{3}DHF^{*}$ was resolved in this study may be interpreted in two **al-** 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 oxygencontaining 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 *(k3)* 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 occuring 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 resonable 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 H_2O_2 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.1° Also, the photosensitized autoxidation of several furans¹¹ has been considered to proceed via O_2 adducts containing ozonide structures like 16. Since the O_2 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.lb and showed the physical and spectroscopic properties reported there.

2-(Naphth-2-yloxy)-3,5,5-trimethyl-2-cyclohexen-l-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 l-(naphth-2-yloxy)-3,4dihydronaphthalene (31, (naphth-2-yloxy)cyclohexylidenephenylmethane (41, 1- (naphth-2-yloxy)-1-phenyl-2-methylethene (5a), and 1-(naphth-**2-yloxy)-l-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! Some experiments were carried out in methanol solution (Merck, Uvasol) which was used without further puri-**

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

Steady Irradiations. Solutions $(5 \times 10^{-3} \text{ M})$ of aryl vinyl ethers in MCH, n-hexane, or methanol/acetic acid/benzene **(1:l:l)** were irradiated in an apparatus described elsewhere.' 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 'H NMR, mass, and IR spectroscopy.

Instruments: Beckman Acta M VI1 UV-spectrophotometer, Varian EM **360** A (60 MHz) and Brucker-Spectrospin **WH-400**

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(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; loa, 75975-23-4; lob, 75975-28-9; 15a, 76024-68-5; 15b, 75975-29-0. 75975-24-5; 11, 75975-25-6; 12, 75975-26-7; 13, 75975-27-8; 14,**

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

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The photocycloaddition reaction of **9,lO-phenanthrenequinone (PQ)** with alicyclic **(la-e)** and bicyclic olefins **(If-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,lOphenanthrenequinone (PQ) with olefins gives mainly two types of products, keto oxetane $2([2, +2]$ addition) and dihydrodioxine $3([4, +2₁]$ addition; eq 1). The relative

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\frac{1}{2} \int_{PQ} \frac{R_1}{R_2} = \frac{1}{2} \int_{PQ} \frac{R_2}{R_1} = \frac{1}{2} \int_{QP} \frac{R_1}{R_2} = \frac{1}{2} \int_{
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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 photoinstability 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.l]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 **345-538.**

⁽²⁾ Farid, *S.;* **Scholz, K.-H.** *Chem. Commun.* **1969,572. (3) Maruyama, K.; Iwai, T.; Naruta, Y.; Otauki, T.; Miyagi, Y.** *Bull. Chem.* **SOC.** *Jpn.* **1978.51, 2052.**