fication. The concentration of aryl vinyl ethers was about 5×10^{-5} M. For low-temperature experiments the cooling technique of Fischer[13] 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 ^{1}H NMR, mass, and IR spectroscopy.

Instruments: Beckman Acta M VII UV-spectrophotometer, Varian EM 360 A (60 MHz) and Brucker-Spectrospin WH-400 (400 MHz) NMR spectrometers, Varian MAT 112 mass spectrometer.

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

Acknowledgment. The author is grateful to Professor G. von Bünau for helpful discussions and to him and to Dr. K. H. Grellmann for critical reading of the manuscript, to Mr. V. Reiffenrath and Mr. N. Müller for technical assistance in the preparative work, and to Dipl.-Chem. P. Schmitt for measuring a 400-MHz NMR spectrum.

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.

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

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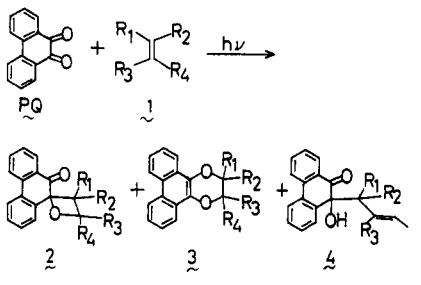
The photocycloaddition reaction of 9,10-phenanthrenequinone (PQ) with alicyclic (**1a–e**) and bicyclic olefins (**1f–l**) was examined upon irradiation with visible light (>420 nm). Alicyclic olefins gave three kinds of products, keto oxetanes (**2**), dihydrodioxines (**3**), and **4**, while bicyclic 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.

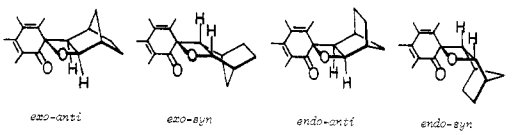
The photocycloaddition reaction of 9,10-phenanthrenequinone (PQ) with olefins gives mainly two types of products, keto oxetane **2** ($[2_\pi + 2_\pi]$ addition) and dihydrodioxine **3** ($[4_\pi + 2_\pi]$ addition; eq 1). The relative



(1)

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.

Chart I



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

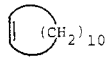
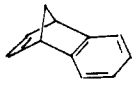
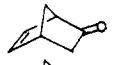
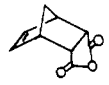
(1) For reviews of photochemical reactions of quinones, see: (a) Pfundt, G.; Schenck, G. O. In "1,4-Cycloaddition"; Hamer, J., Ed.; Academic Press: New York, 1967, pp 345–417; (b) Bruce, J. M. *Q. Rev., Chem. Soc.* **1967**, *21*, 405; (c) Bruce, J. M. In "The Chemistry of Quinonoid Compounds"; Patai,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

0022-3263/81/1946-0983$01.00/0

Table I. Photochemical Reaction of PQ with Cyclic Olefins[a]

entry	olefin	no.	irradn time, h	% yield[b] 2	3	4	others
1		1a	8	18 (17)	0	70 (53)	0
2		1b	21	0	29	59	0
3		1c	26	0	42	34	0
4		1d	42	20 (15)	56 (45)	6	0
5		1e	66	0	46	39	0
6		1f	20	21 (14)[d]	0	0	34 (22)[g]
7		1g	18	89 (77)[e]	0	0	0
8		1h	5	60 (57)[e]	0	0	0
9		1i	8	90 (82)[e]	0	0	0
10		1j	9	83 (66)[f]	0	0	0
11		1k	80[c]	85 (30)[e]	0	0	0
12		1l	40	70 (53)	0	0	0

[a] All reactions were performed upon irradiation of light (>420 nm) from a high-pressure Hg arc lamp in benzene. [b] Yields in parentheses are of isolated product. Others are determined by ^{1}H NMR with *cis*-1,2-dichloroethylene as an internal standard. [c] Acetonitrile was used as solvent. [d] The configuration was not determined. [e] Exo-anti configuration. [f] Mixture of configurational isomers, *exo-anti*-4-oxo/*exo-anti*-5-oxo/*endo-anti*-5-oxo ratio of 35:50:15 (isolated yield). [g] 1,4-Adduct **5** was obtained.

(33 mM) and an olefin (**1a–j** and **1l**, 100 mM) with a light of longer wavelength (>420 nm) using a glass filter (Toshiba color glass filter V-Y 42). The photochemical reaction of olefin **1k** was undertaken in acetonitrile in a similar fashion. Photochemical reactions of five alicyclic olefins and seven bicyclic ones were examined, and four types of the products, **2–5**, were obtained. The results are summarized in Table I.

The ring size of alicyclic olefins affected dramatically the yields of cycloadducts **2** and **3**; of the alicyclic olefins only cyclopentene and cyclooctene gave the corresponding keto oxetanes (entries 1 and 4, in Table I); the others gave only **3** and **4**. In these cases the corresponding keto oxetanes **2** were not found in the detecting limit (>2%) of ^{1}H NMR.

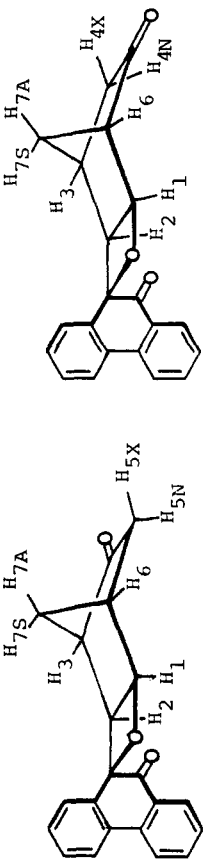
In contrast, bicyclic olefins examined specifically gave keto oxetanes **2f–l** in fair to high yields. Their structures were assigned by inspection of the spectral data; the IR spectrum of **2f–l** commonly showed a conjugate carbonyl absorption at 1690–1705 cm^{-1}. Since these keto oxetanes could have several possible configurations, their structures were determined by ^{1}H NMR as follows. Keto oxetane **2g**[3] was assigned to be the exo-anti form (see Chart I) from ^{1}H NMR and lanthanide-induced shift data. Compound **2h**[4] was also assigned to be an *exo*-keto oxetane; the ^{1}H NMR of **2i** exhibited the characteristics of bridge methylene protons at δ 1.68 (d, 1 H, J = 10 Hz) and 2.94 (d, 1 H, J = 10 Hz), of two bridgehead methine protons at δ 2.91 (s, 1 H) and 3.68 (s, 1 H), of two methine protons at δ 4.86 (d, 1 H, J = 6 Hz) under the influence of an oxygen atom and δ 2.57 (d, 1 H, J = 6 Hz), and of aromatic protons at δ 6.84–7.95 (m, 12 H). The structure assignment of keto oxetane **2j** is more complicated, and eight configurational isomers are expected. However, in actuality three of them (I + II/III ratio of 77:23, total yield 83%) were obtained and isolated by preparative layer chromatography on silica gel (hexane/ether, 50/50). The keto oxetane I contained in the most mobile band was assigned to be *exo-anti*-4-oxo-**2j**; in the ^{1}H NMR spectra, the endo protons of the oxetane ring (H_1 and H_2) do not couple with the bridgehead protons (H_6 and H_3, respectively).[5] One (H_6) of the bridgehead protons couples with an exo methylene proton (H_{5X}, J = 4.5 Hz). The other bridgehead proton (H_3) has no exo protons at the vicinal positions. The ^{1}H NMR data and the lanthanide shift experiment with tris(dipivalomethanato)europium (III) (Eu(DPM)$_3$) are given in Table II. The signals of the protons H_1, H_6, and H_{7s} underwent lager shifts than the protons H_2, H_3, and H_{7A}, respectively. Since it is reasonably concluded that by complexing with

(4) Sasaki, T.; Kanematsu, K.; Ando, I.; Yamashita, O. *J. Am. Chem. Soc.* **1977**, *99*, 871. In this paper the configuration of **2h** is described to be exo. From the comparison of the ^{1}H NMR data with that of **2g**, **2h** is presumed to be exo-anti.

(5) It has been shown by Kumpler[6] that the coupling constants between the endo protons and the bridgehead protons in bicyclo[2.2.1]-heptane system are very small (J = ca. 0 Hz). This phenomenon has been applied to determine the configuration of *exo*- and *endo*-oxetanes.

(6) Kumpler, W. D. *J. Am. Chem. Soc.* **1958**, *80*, 2533.

Table II. Eu(DPM)$_3$-Induced Shift in NMR Spectra of Oxetanes *exo-anti*-4-Oxo-2j and *exo-anti*-5-Oxo-2j[b]



exo-anti-4-oxo-2j

exo-anti-5-oxo-2j

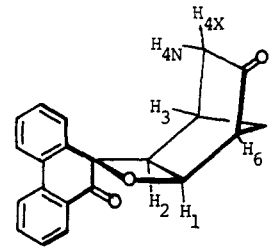
compd	parameter	atom									
		H_1	H_2	H_3	H_{4X}	H_{4N}	H_{5X}	H_{5N}	H_6	H_{7S}	H_{7A}
exo-anti-4-oxo-2j	chemical shift, δ	5.12 (5)	2.84 (5)	3.06 (0)			1.99 (4.5, 18)	1.46 (4.5, 18)	2.34 (4.5)	3.0 (4.5, 11)	1.67 (11)
	(coupling constant, Hz)										
	induced shift,[a] ppm	8.97	7.41	2.18			3.16	3.60	3.66	4.06	1.67
exo-anti-5-oxo-2j	chemical shift, δ	5.20 (5)	2.80 (5)	3.0 (5)	2.08 (5, 18)	1.56 (4.5, 18)			2.25 (0)	3.0 (4.5, 11)	1.57 (11)
	(coupling constant, Hz)										
	induced shift,[a] ppm	10.3	9.89	1.66	2.03	2.31			5.48	4.71	2.99

[a] Determined from the slopes of the plots of shifts (in parts per million) vs. molar ratio of Eu(DPM)$_3$ to keto oxetane by the least-squares method; the concentration of keto oxetane was ca. 0.25 M in $CDCl_3$. [b] Chemical shifts and the induced shifts of aromatic protons are omitted in this table.

the keto oxetanes Eu^{3+} is situated at an equilibrium position between ethereal oxygen and the carbonyl oxygen of quinonoid moiety (not at the carbonyl oxygen on norbornyl ring), the bicyclo[2.2.1]heptane ring is located anti to the quinonoid carbonyl group.

The moderately mobile keto oxetane II on TLC was assigned to be *exo-anti*-5-oxo-**2j**; the ^1H NMR spectra and the lanthanide shift data were similar to those for *exo-anti*-4-oxo-**2j** except for H_3 and H_6. One (H_3) of the bridgehead protons couples with an exo methylene proton (H_{4X}), while the other (H_6) shows no coupling. The larger S value of H_6 than H_3 suggests the carbonyl carbon of norbornyl ring to be at C-5.

The keto oxetane III contained in the least mobile band was assigned to be *endo-anti*-5-oxo-**2j**; the oxetane ring



endo-anti-5-oxo-2j

protons (H_1 and H_2) couple with the bridgehead protons, H_6 (J = 5 Hz) and H_3 (J = 5 Hz), respectively. H_1 and H_2 are exo protons, and the oxetane ring is endo to the norbornyl ring. The bridgehead proton (H_6) has no further coupling, while H_3 couples with H_{4X} (J = 5 Hz). So the carbonyl carbon of the norbornyl ring is at C-5. Since the endo-syn configuration can be excluded because of its steric difficulty, the keto oxetane III is unambiguously assigned to the above configuration.

Compound **2k** was similarly assigned to be exo-anti by comparison of its ^1H NMR spectra with those of other oxetanes. Compound **21** (in this case exo/endo isomers are not present) was assigned to be anti, because the syn isomer may be excluded because of steric difficulties.

Theoretically four stereoisomers are possible for the keto oxetane **2f**, but the exact distinction of them was too difficult to be done only by the spectroscopic method, because only one of the isomers was obtained.

Thermolysis of Keto Oxetanes. Since thermolysis of oxetane was highly sensitive to acidic impurities,[7] that of typical keto oxetanes was performed in *N,N,N',N'*-tetramethylethylenediamine (TMEDA) under an argon atmosphere with the use of sealed glass tubes, which were treated with aqueous KOH solution prior to use. The temperature of the decomposition was separately determined by use of a differential scanning calorimeter (DSC). In every reaction, a starting olefin (**1**) and/or a dihydrofuran (**15**) were obtained. Keto oxetane **2d** gave furan **12** besides the above two products. Formation of dihydrofuran **15** is worthy of a short comment. Though we have no precise evidence, **15** may be afforded by the process given in Scheme I, because some epoxides can lose their oxygen atom in the presence of an oxygen acceptor.[8] PQ, even if generated, was not stable under the present conditions and was not isolated in every reaction mixture. The

(7) (a) Jones, G., II; Staires, J. C. *Tetrahedron Lett.* **1974**, 2099. (b) Imai, T.; Nishida, S. *Chem. Lett.* **1980**, 41.

(8) The photochemical decomposition of aryloxiranes gave the corresponding olefins through the deoxygenation pathway where the radical or zwitterionic intermediate was postulated. See: Becker, R. S.; Bost, R. O.; Kolc, J.; Bertoniere, N. R.; Smith, R. L.; Griffin, G. W. *J. Am. Chem. Soc.* **1970**, *92*, 1302.

Scheme I

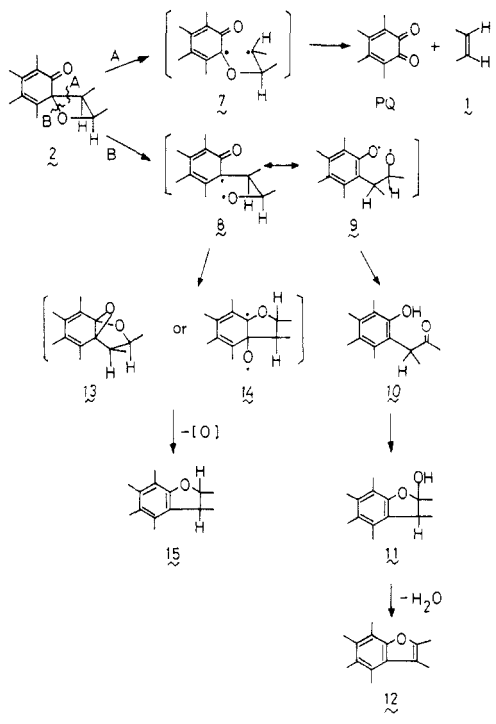


Table III. Thermolysis of Keto Oxetanes 2a,d,g,i,l

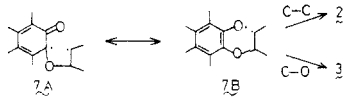
oxetane[d]	temp, °C	% conv	yield, % 1[a]	15[b]	others	A/B path ratio
21	220-230	47	49	trace	0	100/0
2a	270-280	100	42	32	0	57/43
2d	270-280	100	42	33	9[b,c]	50/50
2g	230-245	79	19	58	0	25/75
2i	270-280	100	0	51	0	0/100

[a] Determined by GLC. [b] Determined by NMR. [c] Compound 12. [d] The reaction time was 5 min in each case.

results are summarized in Table III.

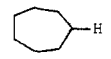
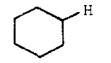
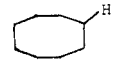
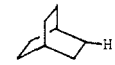
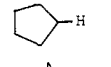
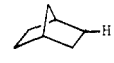
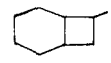
Discussion

The earlier investigations concerning the photochemical cycloaddition of PQ with olefins indicated mostly formation of dihydrodioxines **3**,[9] but doubt was thrown on these results in 1968,[10] since possible formation of oxetanes **2** was suspected. As was shown in our previous[3] and present works, the relative yield of the two products (**2** to **3**) was strongly dependent on the structure of olefins (Table I). Besides **3**, other adducts, **2** and **4**, are the products of photocycloaddition of PQ with *cis*-cyclooctene (entry 4, Table I). In some cases, especially in the reaction with bicyclic olefins, oxetanes **2** were solely isolated as products (entries 6–12). What is the true factor for the determination of the structure of the products? Formation of keto oxetane **2** and dihydrodioxine **3** has been rationally explained in terms of the common biradical intermediate **7**, of which two canonical forms (**7A** and **7B**, eq 2) are possible.



(2)

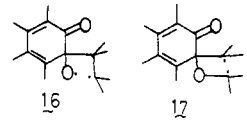
Table IV. $J(^{13}CH)$ for Some C-H Containing Hydrocarbons, $a(\alpha\text{-}^{13}C)$ for the Corresponding Radicals, and the Ratio (2/3) of Photocycloadducts

compd	$J(^{13}CH)$, Hz[a]	$a(\alpha\text{-}^{13}C)$, mT[b]	relative ratio of photocycloadducts 2/3
	123.6 ± 0.2[d,e]	(3.45)	0/100
	124.2 ± 1[c]	4.13 (3.58)	0/100
	123.2 ± 0.2[d,e]	(3.36)	26/74
	127.3 ± 0.1[f]	(4.24)	100/0
	128.6 ± 0.5[c,d]	(4.52)	100/0
	130.3 ± 0.4[f]	(4.88)	100/0
	135[c,d]	(5.89)	100/0

[a] Determined by ^{13}C NMR of parent hydrocarbon (5 M concentration) in $CDCl_3$ at 25 °C. [b] Coupling constants in parentheses are estimated from eq 3. The other is an observed value. See ref 12. [c] For a literature value see ref 18. [d] For a literature value see ref 19. [e] For a literature value see ref 20. [f] For a literature value see ref 21.

sible.[11] As was evident from the experimental results, the ratio **2/3** intensively depends on the structure of the olefins under the conditions applied in the present reactions where successive photolysis of **2** was prohibited. So the fate of the intermediary biradical could be determined by the nature of the olefinic moiety including the unpaired electron, because stability of the quinonoid moiety including the unpaired electron should not be affected by the structure of the olefinic moiety. As was preliminarily pointed out,[3] the most probable relevant factor determining the structure of cycloadducts is likely to be the internal strain of cyclic olefins. Then, the structure of the cycloadduct could be determined by the s character of the unfilled orbital of the olefinic moiety. The s character has been known to relate to the ESR splitting constant $a(\alpha\text{-}^{13}C)$.[12] Moreover, linear correlation between $a(\alpha\text{-}^{13}C)$ for carbon radical (·CH) and $J(^{13}CH)$ for the corresponding hydrocarbon (CH) is established, and they are correlated by eq 3.[12] The estimated $a(\alpha\text{-}^{13}C)$ of some radical fragments employed in the present experiment and the product ratio (**2/3**) are listed in Table IV.

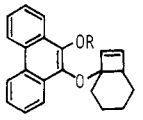
$$a(\alpha\text{-}^{13}C) = 0.214J(^{13}CH) - 23.0 \quad (3)$$



(9) For example, see: Schonberg, A. "Preparative Organic Photochemistry"; Springer-Verlag: New York, 1968; p 119.
(10) See ref 9, p 121.
(11) The chlorine substitution on the expected carbon radical increased oxetane formation. This evidence corresponds to an increase of s character of the unpaired electron on the carbon radical. Farid, S.; Hess, D. *Chem. Ber.* **1969**, 102, 3747.
(12) Dobbs, A. J.; Gilbert, B. C.; Norman, R. O. C. *J. Chem. Soc. A* **1971**, 124.

In fact, the relative ratio 2/3 clearly correlates with the corresponding $a(\alpha\text{-}^{13}C)$. the radical in the olefinic moiety which possesses higher s character provides oxetane predominantly. The similar product selectively in the photocycloaddition of PQ with polychloroethylenes also supports this argument.[11]

The same conclusion was derived from thermolysis of 2, which is best explained as proceeding via the stepwise pathway (A and B in Scheme I) and including two biradical intermediates (7 and 8).[7,13] This method may be most suitable for the evaluation of bond strength. Decomposition of 2 can be initiated by C–C or C–O bond cleavage, which is followed by a second bond fission resulting in the formation of quinone and olefin (path A), by intramolecular hydrogen abstraction to give 12, or by deoxygenation to 15 (path B). The ratio of A/B would reflect the relative bond strength of C–C and C–O in 2. An oxetane containing a higher strained olefin moiety would prefer the C–O bond cleavage rather then the C–C one, because the C–C bond cleavage is characterized by higher s character and higher bond energy compared to those of the unstrained one. The results of the present thermolysis are in good accordance with the s character of an intermediary carbon radical (compare Tables III and IV).



5, R=H

6, R=Ac

Experimental Section

General Methods. Melting points are uncorrected. Proton magnetic spectra were obtained with a JEOL PS-100 spectrometer with tetramethylsilane as an internal standard, and the chemical shifts are reported in δ values. ^{13}C magnetic spectra were obtained with JEOL FX-60 and FX-100 spectrometers. Infrared spectra were measured with a JASCO IRA-1 spectrophotometer. Mass spectra were measured with a Hitachi M-52 mass spectrometer at an ionization potential of 20 eV. Analytical GLC analyses were performed on a JEOL JGC-20K gas chromatograph with a flame-ionization detector. The decomposition temperature was measured with a Du Pont 910 differential scanning calorimeter. Column chromatography was performed by using Wako reagent grade silica gel (100–200 mesh) or Florisil (200 mesh). Analytical and preparative thin-layer chromatographies were performed by using Merck silica gel F-254 (Type 60). Elemental analysis were performed at the Microanalysis Center of Kyoto University.

Materials. 9,10-Phenanthrenequinone (PQ),[14] 5,6-benzobicyclo[2.2.1]hept-2,5-diene (1i),[15] 5-oxobicyclo[2.2.1]hept-2-ene (1j),[16] and bicyclo[4.2.0]oct-2-ene (1f)[17] were synthesized according to the reported method. The other olefins were commercially available and were used without further purification. Benzene was freshly distilled from benzophenone ketyl and stored under a nitrogen atmosphere. Acetonitrile was distilled from phosphorus pentoxide and stored under a nitrogen atmosphere. *N,N,N',N'*-Tetramethylethylenediamine (TMEDA) was dried over potassium hydroxide and then distilled.

Photochemical Reaction of PQ with Olefins. General Method. A mixture of PQ (1.0 mmol, 208 mg) and an olefin (1, 3.0 mmol) in 30 mL of benzene or acetonitrile was irradiated with a high-pressure mercury arc lamp filtered with a Toshiba color glass filter, Type V-Y 42. The progress of the reaction was traced by disappearance of PQ by TLC analysis. The solvent was evaporated in vacuo, and the yields of the products were determined by ^1H NMR with *cis*-1,2-dichloroethylene as an internal standard. The crude products were chromatographed either on Florisil eluted with benzene or on silica gel eluted with dichloromethane.

Entry 1. A benzene solution (30 mL) of PQ (1.0 mmol, 208 mg) and cyclopentene (1a; 3.0 mmol, 204 mg) was irradiated for 8 h. After evaporation of the solvent, NMR analysis indicated the presence of two compounds: 2a (18%) and 4a (70%). The products were separated by column chromatography on silica gel eluted with dichloromethane. The first fraction contained 4a as mixture of two diastereomeric isomers: pale yellow cubes; mp 76–77 °C (dichloromethane–hexane); IR (KBr) 3490, 1680, 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.41–2.31 (m, 4 H, CH_2CH_2), 2.96 (m, 1 H, methine H), 3.86 and 4.02 (2 s in a ratio of 1:1, 1 H, OH), 5.22 (m, 1 H, olefinic H), 5.70 (m, 1 H, olefinic H), 7.23–7.83 (m, 8 H, aromatic H).

Anal. Calcd for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84. Found: C, 82.62; H, 6.08.

The second fraction contained 2a: 47 mg (17%); colorless needles; mp 143–144 °C (hexane–ether); IR (KBr) 1705, 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.20–2.30 (m, 6 H, $(CH_2)_3$), 3.15 (m, 1 H, H on oxetane β-C), 5.51 (dd, 1 H, H on oxetane α-C, J = 4 and 4.5 Hz), 7.20–7.92 (m, 8 H, aromatic H); mass spectrum, m/e (relative intensity) 208 (50), 180 (base).

Anal. Calcd for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84. Found: C, 82.56; H, 6.14.

Entry 2. A benzene solution (30 mL) of PQ (1.0 mmol, 208 mg) and cyclohexene (1b; 3.0 mmol, 246 mg) was irradiated for 21 h. After evaporation of the solvent, NMR analysis indicated the presence of two compounds: 3b[3] (29%) and 4b[3] (59%)

Entry 3. A benzene solution (30 mL) of PQ (1.0 mmol, 208 mg) and cycloheptene (1c; 3.0 mmol, 288 mg) was irradiated for 26 h. After evapolation of solvent, NMR analysis indicated the presence of two compounds: 3c[3] (42%) and 4c[3] (34%).

Entry 4. A benzene solution (30 mL) of PQ (1.0 mmol, 208 mg) and cyclooctene (1d; 3.0 mmol, 330 mg) was irradiated for 42 h. After evaporation of the solvent, NMR analysis indicated the presence of three compounds: 2d (20%), 3d (56%), and 4d (6%). The products were separated by column chromatography on Florisil eluted with benzene. The first fraction contained 3d (143 mg, 45%).[3] The second fraction contained 4d.[3] The third fraction contained 2d (48 mg, 15%).[3]

Entry 5. A benzene solution (30 mL) of PQ (1.0 mmol, 208 mg) and cyclododecene (1e; 3.0 mmol, 498 mg) was irradiated for 66 h. After evaporation of the solvent, ^1H NMR analysis indicated the presence of two compounds: 3e[3] (46%) and 4e[3] (39%).

Entry 6. A benzene solution (30 mL) of PQ (1.0 mmol, 208 mg) and bicyclo[4.2.0]oct-2-ene (1f; 3.0 mmol, 324 mg) was irradiated for 20 h. After evaporation of solvent, ^1H NMR analysis indicated the presence of keto oxetane 2f (21%) and 1,4-adduct 5 (34%). The products were separated by column chromatography on Florisil eluted with benzene. The first fraction contained 5: 66 mg (22%); colorless oil; IR (neat) 3520, 3030, 2930, 2840, 1620, 1600, 1500, 1475, 1450, 1335, 1285, 1215, 1160, 1110, 1045, 1015, 750, 715 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.0–2.6 (m, 8 H, CH_2), 3.25 (br t, 1 H, CH, $J \simeq 4$ Hz), 5.99 (dd, 2 H, olefinic H, J = 7 Hz), ~6.2 (br, 1 H, OH), 7.2–7.8 (m, 4 H, arom H), 7.92–8.02 (m, 1 H, arom H), 8.17–8.28 (m, 1 H, arom H), 8.46–8.56 (m, 2 H, arom H); ^{13}C NMR ($CDCl_3$) δ 17.98 (t), 18.22 (t), 23.43 (t), 47.90 (d), 88.10 (s), 122.06, 122.36, 122.41, 122.55, 123.97, 125.43 (s), 126.06, 126.30, 126.35 (s), 130.34 (s), 131.32 (s), 138.39 (d), 140.28 (s), 141.56 (d), 142.09 (s); mass spectrum, m/e (relative intensity) 316 (P, 41), 298 (19), 257 (19), 211 (97), 181 (base), 107 (53).

Since 5 was unstable and easily decomposed to PQ and unassignable material during purification, acetylation of 5 by Ac_2O

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and pyridine at room temperature for 5 h followed by the usual workup gave the corresponding monoacetate **6**: colorless oil; IR (neat) 3030, 2930, 1765, 1615, 1600, 1490, 1475, 1450, 1365, 1325, 1200, 1155, 1100, 1050, 1030, 750, 720, 670 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.36–2.5 (m, 8 H, CH_2), 2.45 (s, 3 H, CH_3), 3.12 (m, 1 H, CH, $J \simeq 4$ Hz), 5.95–6.07 (dd, 2 H, olefinic H, $J = 7$ Hz), 7.48–7.62 (m, 4 H, arom H), 7.76–7.88 (m, 1 H, arom H), 8.12–8.26 (m, 1 H, arom H), 8.49–8.63 (m, 2 H, arom H); mass spectrum, *m/e* (relative intensity) 358 (P, 14), 315 (21), 351 (18), 210 (base), 141 (53), 107 (25).

Anal. Calcd for $C_{24}H_{22}O_3$: C, 80.42; H, 6.19. Found: C, 80.16; H. 6.20.

The second fraction of the reaction mixture contained **2f**: 44 mg (14%); colorless cubes; mp 118–119.5 °C; IR (CCl_4) 2925, 1700, 1600, 960 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.2–1.8 (m, 8 H, CH_2), 2.55–2.95 (m, 2 H, CH), 3.00 (dd, 1 H, H on oxetane β-C, $J = 3, 4$ Hz), 5.02 (d, 1 H, H on oxetane α-C, $J = 4$ Hz), 7.32–8.13 (m, 8 H, arom H); mass spectrum, *m/e* (relative intensity) 316 (P, 10), 234 (25), 208 (20), 180 (base).

Anal. Calcd for $C_{22}H_{20}O_2$: C, 83.51; H, 6.37. Found: C, 83.75; H, 6.42.

Entry 7. A benzene solution (30 mL) of PQ (1.0 mmol, 208 mg) and bicyclo[2.2.1]hept-2-ene (**1g**; 3.0 mmol, 282 mg) was irradiated for 18 h. After evaporation of the solvent, NMR analysis indicated the presence of keto oxetane **2g** (89%).[3] Column chromatography on silica gel eluted with dichloromethane afforded **2g** (232 mg, 77%).

Entry 8. A benzene solution (30 mL) of PQ (1.0 mmol, 208 mg) and bicyclo[2.2.1]hept-2,5-diene (**1h**; 3.0 mmol, 276 mg) was irradiated for 5 h. After evaporation of the solvent, NMR analysis indicated the presence of keto oxetane **2h** (60%).[4] Column chromatography on silica gel eluted with dichloromethane afforded **2h** (171 mg, 57%).

Entry 9. A benzene solution (30 mL) of PQ (1.0 mmol, 208 mg) and 5,6-benzobicyclo[2.2.1]hept-2,5-diene (**1i**; 3.0 mmol, 427 mg) was irradiated for 8 h. After evaporation of the solvent, NMR analysis indicated the presence of keto oxetane **2i** (90%). Column chromatography on silica gel eluted with dichloromethane afforded **2i**: 287 mg (82%); colorless cubes; mp 208–210 °C (hexane–ether); IR (KBr) 1695, 1595, 950 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.68 (d, 1 H, bridge CH_2, $J = 10$ Hz), 2.57 (d, 1 H, H on oxetane β-C, $J = 6$ Hz), 2.91 (s, 1 H, bridgehead H), 2.94 (d, 1 H, bridge CH_2, $J = 10$ Hz), 3.68 (s, 1 H, bridgehead H), 4.86 (d, 1 H, H on oxetane α-C, $J = 6$ Hz), 6.84–7.95 (m, 12 H, aromatic H); mass spectrum, *m/e* (relative intensity) 350 (P, base), 180 (93), 142 (33), 141 (15).

Anal. Calcd for $C_{25}H_{18}O_2$: C, 85.69; H, 5.18. Found: C, 85.49; H, 5.46.

From the comparison of chemical shift of the bridgehead methylene proton H_{7S} (δ 1.78 in **2g** and δ 1.68 in **2i**), the configuration was expected to be exo-anti.

Entry 10. A benzene solution (30 mL) of PQ (1.0 mmol, 208 mg) and 5-oxobicyclo[2.2.1]hept-2-ene (**1j**; 3.0 mmol, 324 mg) was irradiated for 9 h. After evaporation of the solvent, NMR analysis indicated the presence of three isomeric keto oxetanes, I plus II (64%) and III (19%). Preparative layer chromatography on silica gel eluted with hexane–ether (50:50) gave three pure products. The R_f 0.25 band contained I (74 mg, 23%), which was assigned to be *exo-anti*-4-oxo-**2j** by a lanthanide shift experiment: pale yellow cubes; mp 166–167 °C; IR (KBr) 1740, 1700, 1595, 970 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.46 (dd, 1 H, H_{5N}, $J = 4.5, 18$ Hz), 1.67 (d, 1 H, H_{7A}, $J = 11$ Hz), 1.99 (dd, 1 H, H_{5X}, $J = 4.5, 18$ Hz), 2.34 (m, 1 H, H_6, $J = 4.5$ Hz), 2.84 (d, 1 H, H_2, $J = 5$ Hz), ~3.0 (dm, 1 H, H_{7S}, $J = 4.5, 11$ Hz), 3.06 (s, 1 H, H_3), 5.12 (d, 1 H, H_1, $J = 5$ Hz), 7.3–8.0 (m, 8 H, aromatic H); mass spectrum, *m/e* (relative intensity) 316 (P, 8), 208 (base), 180 (50), 76 (77).

Anal. Calcd for $C_{21}H_{16}O_3$: C, 79.73; H, 5.10. Found: C, 79.90; H, 5.04.

The R_f 0.20 band contained II (101 mg, 32%), which was assigned to be *exo-anti*-5-oxo-**2j** by a lanthanide shift experiment: pale yellow cubes; mp 191–192 °C; IR (KBr) 1740, 1700, 1595, 985 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.56 (dd, 1 H, H_{4N}, $J = 4.5, 18$ Hz), 1.57 (d, 1 H, H_{7A}, $J = 11$ Hz), 2.08 (dd, 1 H, H_{4X}, $J = 5, 18$ Hz), 2.25 (s, 1 H, H_6), 2.80 (d, 1 H, H_2, $J = 5$ Hz), ~3.0 (m, 1 H, H_3, $J = 5$ Hz), ~3.0 (dm, 1 H, H_{7S}, $J = 4.5, 11$ Hz), 5.20 (d, 1 H, H_1, $J = 5$ Hz), 7.3–8.0 (m, 8 H, aromatic H); mass spectrum, *m/e* (relative intensity) 316 (P, 10), 208 (base), 180 (36), 76 (45).

Anal. Calcd for $C_{21}H_{16}O_3$: C, 79.73; H, 5.10. Found: C, 79.65; H, 5.28.

The R_f 0.15 band contained III (32 mg, 10%), which was assigned to be *endo-anti*-5-oxo-**2j**: pale yellow cubes; mp 193–194 °C (hexane–dichloromethane); IR (KBr) 1750, 1690, 1600, 960 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.38 (dd, 1 H, H_{7S}, $J = 4.5, 11$ Hz), 1.85 (dd, 1 H, H_{4H}, $J = 5, 18$ Hz), 1.79 (d, 1 H, H_{7A}, $J = 11$ Hz), 2.62 (dd, 1 H, H_{4N}, $J = 4.5, 18$ Hz), 2.78 (dd, 1 H, H_3, $J = 5, 5$ Hz), 3.11 (d, 1 H, H_6, $J = 5$ Hz), 3.21 (dd, 1 H, H_2, $J = 5, 8$ Hz), 5.44 (dd, 1 H, H_1, $J = 5, 8$ Hz), 7.30–7.96 (m, 8 H, aromatic H); mass spectrum, *m/e* (relative intensity) 316 (P, 14), 208 (base), 180 (57), 76 (64).

Anal. Calcd for $C_{21}H_{16}O_3$: C, 79.73; H, 5.10. Found: C, 79.59; H, 5.08.

Entry 11. An acetonitrile solution (30 mL) of PQ (1.0 mmol, 208 mg) and bicyclo[2.2.1]hept-2-ene-5,6-dicarboxylic acid anhydride (**1k**; 3.0 mmol, 492 mg) was irradiated for 80 h. After evaporation of the solvent, NMR analysis indicated the presence of keto oxetane **2k** (85%). Column chromatography on Florisil eluted with dichloromethane afforded **2k**: 112 mg (30%); colorless cubes; mp 192–193 °C (hexane–dichloromethane); IR (KBr) 1730, 1700, 1240, 1000 cm^{-1}; ^1H NMR (acetone-d_6) δ 1.68 (d, 1 H, bridge CH_2, $J = 10.5$ Hz), 2.34 (d, 1 H, bridgehead CH, $J = 4$ Hz), 2.64 (d, 1 H, H on oxetane β-C, $J = 4$ Hz), 2.91 (d, 1 H, bridge CH_2, $J = 10.5$ Hz), 3.15 (d, 1 H, bridgehead CH, $J = 4$ Hz), 3.51 (m, 2 H, CH-COO), 4.86 (d, 1 H, H on oxetane α-C, $J = 4$ Hz), 7.20–7.86 (m, 8 H, aromatic H); mass spectrum, *m/e* (relative intensity) 372 (P, 10), 208 (50), 180 (base).

Anal. Calcd for $C_{23}H_{16}O_5$: C, 74.18; H, 4.33. Found: C, 73.85; H, 4.28.

Entry 12. A benzene solution (30 mL) of PQ (1.0 mmol, 208 mg) and bicyclo[2.2.2]oct-2-ene (**11**; 3.0 mmol, 324 mg) was irradiated for 40 h. After evaporation of the solvent, NMR analysis indicated the presence of **21** (70%). Column chromatography on silica gel eluted with dichloromethane afforded **21**: 167 mg (53%); colorless cubes; mp 133–134 °C; IR (KBr) 1695, 1590, 945 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.0–2.4 (m, 8 H, CH_2CH_2), 1.60 (m, 1 H, bridgehead CH), 1.92 (m, 1 H, bridgehead CH), 3.72 (dd, 1 H, H on oxetane β-C, $J = 3, 7.5$ Hz), 5.02 (dd, 1 H, H on oxetane α-C, $J = 3, 7.5$ Hz), 7.3–8.1 (m, 8 H, aromatic H); mass spectrum, *m/e* (relative intensity) 316 (P, 50), 208 (35), 180 (base).

Anal. Calcd for $C_{22}H_{20}O_2$: C, 83.51; H, 6.37. Found: C, 83.58; H, 6.43.

Thermolysis of Oxetane. General Methods. After being boiled in 10% aqueous KOH solution for 10 h, sealed Pyrex tubes were washed with water and dried. The mixture of a keto oxetane (0.2–0.4 mmol) and TMEDA (an equimoler amount with the corresponding keto oxetane) was sealed in a Pyrex tube under an argon atmosphere and was heated in oil bath at an appropriate temperature for 5 min. The reaction mixture was passed through a silica gel layer and eluted with benzene (**2a**) or dichloromethane (**2d,g,i,l**). The olefin was analyzed by GLC, and the other products were analyzed by NMR using *cis*-1,2-dichloroethylene as an internal standard.

A. Thermolysis of 2a. The mixture of **2a** (0.35 mmol, 97 mg) and TMEDA (40 mg) was heated at 270–280 °C for 5 min. After separation of tar by column chromatography on silica gel eluted with benzene, GLC and NMR analysis indicated the presence of **1a** (42%) and **15a** (32%). For **15a**: colorless cubes; mp 119–121 °C (hexane–dichloromethane); IR (KBr) 1635, 1605 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.62–2.37 (m, 6 H, CH_2CH_2), 4.26 (m, 1 H, H on dihydrofuran β-C), 5.55 (m, 1 H, H on dihydrofuran α-C), 7.23–7.77 (m, 5 H, aromatic H), 8.01–8.10 (m, 1 H, aromatic H), 8.58–8.70 (m, 2 H, aromatic H); mass spectrum, *m/e* (relative intensity) 260 (P, base), 231 (60).

Anal. Calcd for $C_{19}H_{16}O$: C, 87.66; H, 6.19. Found: C, 87.44; H, 6.08.

B. Thermolysis of 2d. The mixture of **2d** (0.39 mmol, 124 mg) and TMEDA (45 mg) was heated at 270–280 °C for 5 min. After separation of tar by column chromatography on silica gel with dichloromethane, GLC and NMR analysis indicated the presence of **1d** (42%), **15d** (33%), and **12** (9%). Preparative layer chromatography on silica gel eluted with hexane gave pure **15d** and **12**. The R_f 0.20 band contained **12**.[3] The R_f 0.10 band contained **15d**: colorless cubes; mp 107–109 °C; IR (KBr) 1635, 1610 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.10–2.39 (m, 12 H, CH_2CH_2), 3.60

(m, 1 H, H on dihydrofuran β-C), 4.80 (dd, 1 H, H on dihydrofuran α-C, J = 7, 15 Hz), 7.41–7.62 (m, 5 H, aromatic H), 4.98–8.07 (m, 1 H, aromatic H), 8.49–8.67 (m, 2 H, aromatic H); mass spectrum, m/e (relative intensity) 302 (P, base), 260 (15), 141 (80).

Anal. Calcd for $C_{22}H_{22}O$: C, 87.37; H, 7.33. Found: C, 87.54; H, 7.28.

C. Thermolysis of 2g. The mixture of **2g** (0.20 mmol, 60.4 mg) and TMEDA (23 mg) was heated at 230–245 °C for 5 min. After separation of tar by column chromatography on silica gel with dichloromethane, GLC and NMR analysis indicated the presence of **1g** (19%) and **15g** (58%).[3]

D. Thermolysis of 2i. The mixture of **2i** (0.20 mmol, 70 mg) and TMEDA (23 mg) was heated at 270–280 °C for 5 min. After separation of tar by column chromatography on silica gel with dichloromethane, NMR analysis indicated the presence of **15i**: 51% yield; colorless cubes; mp 84–85 °C (hexane); IR (CCl_4) 1630, 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.88 (d, 1 H, bridge CH_2, J = 10 Hz), 2.07 (d, 1 H, bridge CH_2, J = 10 Hz), 3.73 (s, 1 H, bridgehead CH), 3.79 (s, 1 H, bridgehead CH), 3.94 (d, 1 H, H on dihydrofuran β-C, J = 8 Hz), 5.17 (d, 1 H, H on dihydrofuran α-C, J = 8 Hz), 7.08–8.15 (m, 10 H, aromatic H), 8.54–8.65 (m, 2 H, aromatic H); mass spectrum, m/e (relative intensity) 334 (P, 25), 209 (50), 117 (100).

Anal. Calcd for $C_{25}H_{18}O$: C, 89.79; H, 5.43. Found: C, 90.03; H, 5.64.

E. Thermolysis of 21. The mixture of **21** (0.40 mmol, 127 7g) and TMEDA (46 mg) was heated at 220–230 °C for 5 min. After separation of tar by column chromatography on silica gel with dichloromethane, GLC analysis indicated the presence of **11** (49%).

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Registry No. 1a, 142-29-0; **1b**, 110-83-8; **1c**, 628-92-2; **1d**, 931-87-3; **1e**, 1501-82-2; **1f**, 616-10-4; **1g**, 498-66-8; **1h**, 121-46-0; **1i**, 4453-90-1; **1j**, 694-98-4; **1k**, 2746-19-2; **1l**, 931-64-6; **2a**, 76036-53-8; **2d**, 68461-98-3; **2f**, 76036-54-9; **2g**, 68509-94-4; **2h**, 76094-33-2; **2i**, 76036-55-0; *exo-anti*-4-oxo-**2j**, 76036-56-1; *exo-anti*-5-oxo-**2j**, 76036-57-2; *endo-anti*-5-oxo-**2j**, 76094-34-3; **2k**, 76036-58-3; **2l**, 76036-59-4; **3b**, 76036-60-7; **3c**, 76036-61-8; **3d**, 76036-62-9; **3e**, 76094-35-4; **4a** (isomer 1), 76036-63-0; **4a** (isomer 2), 76036-64-1; **4b**, 58447-89-5; **4c**, 58447-90-8; **4d**, 58447-91-9; **4e**, 68461-96-1; **5**, 76036-65-2; **6**, 76036-66-3; **12**, 68462-00-0; **15a**, 76036-67-4; **15d**, 76036-68-5; **15g**, 68461-99-4; **15i**, 76036-69-6; PQ, 84-11-7.

Photochemistry of Stable Pyridinyl Radicals. Photolysis of *N*-Alkyl-4-(carboalkoxy)pyridinyls[1]

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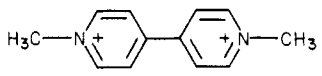
Photoinduced decomposition of *N*-benzyl-4-carbethoxypyridinyl (**1a**), *N*-methyl- (**1b**) and *N*-benzyl-4-(carbomethoxy)pyridinyl (**1c**), and their mixture was studied in degassed acetonitrile. *N*-Benzyl homologues (**1a** and **1c**) were smoothly photolyzed to ethyl (or methyl) isonicotinate by loss of a benzyl group, whereas the *N*-methyl homologue (**1b**) was comparatively stable toward UV light; the rate of disappearance of **1c** relative to that of **1b** was 11:1. A mechanism is postulated, which involves the formation of an alkyl radical by C–N bond homolysis followed by attack on the pyridinyl radical to form dihydropyridines. This is supported by a plot of the yield of ethyl isonicotinate vs. the ratio of initial concentrations $[\mathbf{1b}]_0/[\mathbf{1a}]_0$. Pyridinyl radicals **1** possess their absorption maxima at around 300, 395, and 630 nm; those at 300 and 395 nm maxima participate in this reaction.

Pyridinium ions in general act as excellent electron acceptors. For example, the bis(methyl quaternary salt) of 4,4'-dipyridyl, so called methyl viologen (MV^{2+}), has often



MV^{2+}

been employed as an electron trapper in order to ascertain whether visible light-induced electron transfer may occur in a certain artificial photosynthesis.[2]

The photochemical behavior of stable pyridinyl radicals is an intriguing subject, because their photostability is an essential factor for the acceptor. In our preliminary experiment, the radical cation of benzyl viologen ($BV^{+\cdot}$) was observed to decompose by UV light on the basis of the fact that its characteristic blue color fades on irradiation.[3] A simpler pyridinyl radical is preferable to the study of the photochemistry of the radicals because of the formation of complex products from $BV^{+\cdot}$. Simple and stable pyridinyl radicals were first isolated by Kosower et al.[4] in the reduction of monopyridinium ions with zinc powder. Little data are available on the photochemistry of this stable radical except that *N*-ethyl-4-(carbomethoxy)pyridinyl radical induces polymerization of benzaldehyde under the influence of light.[5,6]

We disclose the photochemical behavior of this pyridinyl radical as a first step in the study of the photochemistry of these electron trappers.

(1) Contribution no. 275.

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(6) Irradiation of **1c** was independently done by Ikegami et al.[7] They obtained the spectral evidence for benzyl radical from low-temperature photolysis of **1c** at 77 K, but their attention was mainly focused on its photophysical processes.

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