Photoaddition Reaction of 9,10-Phenanthrenequinone with Alicyclic Olefins.[1] Product Distribution

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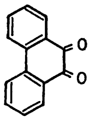
(Received July 21, 1977)

The phtoaddition reaction of 9,10-phenanthrenequinone (**1**) with several alicyclic olefins (**6**) has been investigated. In addition to the expected products, dihydrodioxin(**2**) and keto oxetane (**3**), the hydroxydihydrofuran derivative (**4**, **5**) were found. Product distribution was shown to be deeply dependent on the structure of the olefins. Product **4** has been shown to be produced *via* the photorearrangement of **3**.

9,10-Phenanthrenequinone (PQ) **1** photochemically adds to olefins to give several products. Schönberg and Mustafa reported first the photochemical reaction of **1** with olefins gave dihydrodioxin **2**. The subsequent reaction has been investigated by many workers.[2—6] According to the literature[7] the product distribution is dependent on the olefins used in the reaction. For example, dihydrodioxin **2**, a common product in the reaction with acyclic olefins, is the exclusive product in the reaction of **1** with either *cis*- or *trans*-stilbens.[8] In contrast, the reactions with benzofuran,[9] isocumarin,[9] and vinylene carbonate[5,10] afforded keto oxetanes as the major products.

In this investigation the chemical reaction of **1** with alicyclic olefin **6** of various ring sizes from six to twelve membered has been examined. A novel type of product **4** has been isolated and the amounts of **4** were found to be dependent on the structure of the olefins.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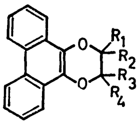

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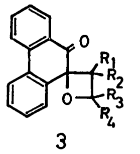

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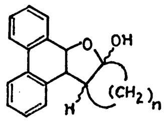

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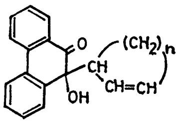

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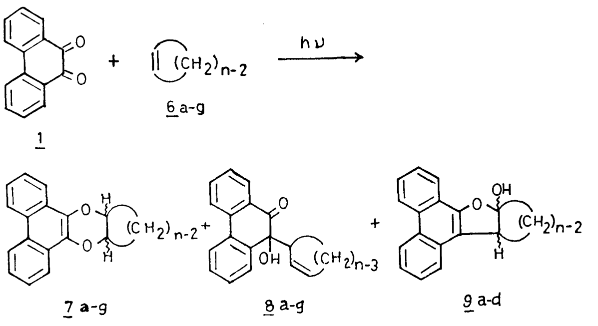
Results

*Photochemical Reactions of 9,10-Phenanthrenequinone **1** with Alicyclic Olefins **6a—g**.* Irradiation of a benzene solution of **1** and **6a—g** in a Pyrex tube using a 300W high pressure Hg lamp gave three kinds of products **7**, **8**, and **9**. Under these conditions no keto oxetane was found. The keto oxethane was obtained (yield 18%), however, using light of wavelength longer than 400 nm in the reaction of **1** with **6c**.

The formation of dihydrodioxin **7** has been reported in many photochemical reactions of **1** with olefins.[2—6] However, the products of adduct **8** type have been found only in a few cases.[11] So far hydroxydihydrofuran **9** has never been described in the literature. The structure of these products has been determined on the basis of their spectral data and yields are given in Table 1. Although the dihydrodioxins **7a**—**g** consisted of a mixture of the *cis*- and *trans*-isomers, the two isomers were separated in some cases by fractional crystallization. The isomer ratios were determined, in general, by means of ^{1}H-NMR spectroscopy taking advantage of the bridge-head methine protons exhibiting two distinct signals. The ^{1}H-NMR signal at lower field has been assigned to the *cis*-isomer and that at higher field to the *trans*-isomer.[12] It has been found that, in the conformational equilibrium that the bridge-head proton of the *trans*-isomer is advantageous to take axial position (Fig. 1); The *cis*-isomer favors the equatorial position, where it is affected strongly by the anisotropic effect of the dihydrodioxin ring.



a; n=6, **b**; n=7, **c**; n=8, **d**; n=9, **e**; n=10, **f**; n=11 **g**; n=12.

As a result, the bridge-head proton of the *cis*-isomer appears at lower field. Table 2 shows the isomer ratios of the dihydrodioxins **7a**—**g**.

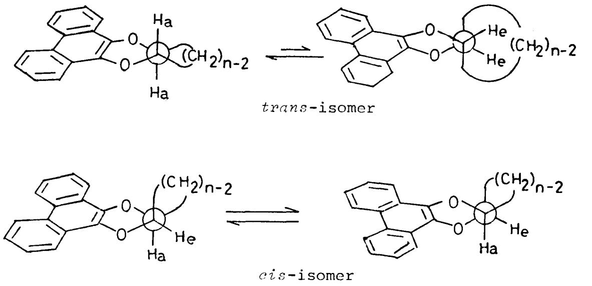


Fig. 1. The conformational equilibrium of *cis*- and *trans*-dihydrodioxins.

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Table 1. The yields of photoproducts[a)]

Olefin		Products		
		$7^{b)}$	$8^{c)}$	9
6a;	$n=$ 6	46%	42% (mp 75—76 °C)	2% (mp 142—143 °C)
b	$7^{e)}$	54%	23% (mp 90—93 °C)	8% (mp 154—155 °C)
c	$8^{e)}$	66%	6% (oil)	20% (mp 149—150 °C)
d	$9^{e)}$	59%	8% (oil)	7% (mp 129—130 °C)
e	$10^{e)}$	42%	32% (mp 115—118 °C)	—[d)]
f	$11^{e)}$	35%	38% (oil)	—[d)]
g	$12^{f)}$	42%	40% (oil)	—[d)]

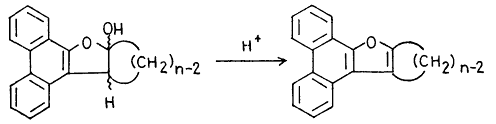
a) Yields were calculated on the basis of PQ used. b) Mixture of two isomers. c) Mixture of two or four isomers. d) Hydroxydihydrofuran was not isolated. e) *cis*-Isomer was used in the reaction. f) A mixture of *cis*- and *trans*-isomers was used in the reaction.

Table 2. The isomer ratios of dihydrodioxin **7**

Dihydro-dioxin	Ring size of alicyclic olefin	*cis*-Isomer (%)	*trans*-Isomer (%)
7a	6	85 (4.08[a)], oil[b)])	: 15 (3.48, oil)
b	7	69 (4.25, oil)	: 31 (3.70, mp 189.5—192 °C)
c	8	70 (4.41, mp 93.5—96 °C)	: 30 (4.00, oil)
d	9	88 (4.56, mp 124—6 °C)	: 12 (4.20, oil)
e	10	82 (4.61)[c)]	: 18 (4.24)[c)]
f	11	49 (4.56, mp 170—2 °C)	: 51 (4.24, mp 236.5—237.5 °C)
g	12	48 (4.52, mp 185—191 °C[d)])	: 52 (4.24, mp 220 °C[d)])

a) Chemical shifts of bridge-head methine protons. b) Physical properties. c) *cis*- and *trans*-mixture, mp 145—152 °C. d) A small amount of another isomer was contained. e) Not isolated.

Adducts **8a**—**c**, which arose from the α-hydrogen abstraction from the olefinic double bond, are mixtures of two diastereomers. Therefore, **8a** and **8b** show two distinguishable ^{1}H-NMR absorption signals which can be assigned to each of the diastereomer's. In the case of **8c**, the two diastereomers could not be distinguished by ^{1}H-NMR spectroscopy. Such phenomena have been observed by other investigators in the photochemical reactions of 1,1,4,4-tetramethyltetralin-2,3-dione, 1,1,4,4-tetramethylcyclohexane-2,3-dione, and 1,1-dimethylindan-2,3-dione with cyclohexene.[13)] Adducts **8d**—**g** were isolated respectively as a mixture of four geometrical isomers in cycloalkene moiety. Hydroxydihydrofurans **9c** and **9d** can be easily dehydrated in the presence of a trace amount of acid. Dehydration in acidified methanol gave **10c** and **10d** in nearly quantitative yield. The dehydration strongly supports the structure of **9**. Under neutral conditions **9c, d** are fairly stable, but **9a, b** are not, decomposing to yield unidentifiable products.



9c,d 10c,d

*Photochemical Reaction of **1** with Norbornene **11**.*

The major products of the photoreaction of **1** with cycloalkenes **6a**—**g** as described above are the dihydrodioxines **7a**—**g**. In the photoreaction of **1** with norbornene **11** only the oxetane **12** was produced (yield: 75%), consequently the structure of the oxetane product has to be either **12A** or **B**. The configuration of the obtained oxetane **12** was determined by ^{1}H-NMR spectrocsopy: H_1' proton (δ 4.8, d, $J=5$ Hz) couples with H_2' proton (δ 2.42, d, $J=5$ Hz) and *vice versa.* However, the *endo* protons, H_1' and H_2', do not couple with the bridge-head protons, H_6' and H_3', respectively. It has been shown by Kumpler[14)] that the coupling constants between the *endo* protons and the bridge-head protons in bicyclo[2.2.1]heptane system are very small ($J=ca.$ 0). This phenomenon has been applied to determine the configuration of *exo*- and *endo*-oxetanes which were obtained from the photochemical reaction of norbornene with acetylcyanide.[15)] From this evidence the configuration of the obtained oxetane **12** has been set as *exo*, *cis*. The orientation of the bicyclo[2.2.1]heptane ring to the C=O group in **12** has been determined from lantanide induced shift data. The shifts of the proton signals due to complex formation with tris(dipivalometanato)europium(III) [Eu(DPM)$_3$][16)] are given in Table 3. The signals of the protons, H_1', H_6', and H_{7s}' underwent larger shifts than those of the protons, H_2', H_3', and H_{7a}', respectively. In addition, the same induced shift values were observed for each of the *endo* protons, H_{4N}' and H_{5N}'.

Phenanthrenequinone **1** + Nornene **11** ⟶ **12A** + **12B**

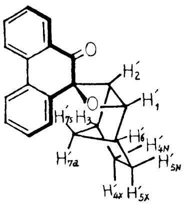
Similarly, the two *exo* protons, H_{4x}' and H_{5x}', showed the same induced shift. The induced shift values of the oxetane ring α- and β-protons are small compared with the corresponding oxetane ring protons of **15**. In the investigation of the structure of **15** it has been shown that the Eu^{3+} ion in the complex predominantly

TABLE 3. $Eu(DPM)_3$ INDUCED SHIFTS[a] IN THE ^1H-NMR SPECTRUM OF 12[c]

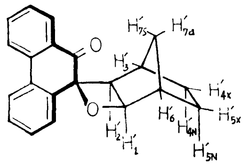
Proton	H'_1	H'_2	H'_3	H'_{4X} and H'_{5X}	H'_{4N} and H'_{5N}	H'_6	H'_{7s}	H'_{7a}
Chemical shift[b] ppm	4.80	2.42	2.55	1.08	0.77	2.55	1.78	1.30
Induced shift ppm	18.4	15.0	2.1	1.2	3.9	7.2	7.0	3.7

a) Determined from the slopes of the plots of shifts (in ppm) *vs.* molar ratio of $Eu(DPM)_3$: **12** by least-squares method; concentration of **12**, *ca.* 0.125 M in CCl_4. b) CCl_4 was used as the solvent. c) The Chemical shifts and the induced shifts of aromatic protons are omitted in this table.

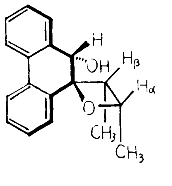
associates with the ethereal oxygen rather than with the alcohlic oxygen.[5] Moreover, in **12** the C-8 proton undergoes a smaller shift than that of the C-8 proton of **15**. Consequently, it has been concluded that by complexing with **12** the Eu^{3+} is situated at an equilibrium position between the ethereal oxygen and the carbonyl oxygen and the bicyclo[2.2.1]heptane ring is located *trans* to the carbonyl group; the isolated one corresponds to **12A**. The same conclusion may be drawn on the basis of the down-field shift of the *syn* proton H'_{7s}, compared with the *anti* proton, H'_{7a}, interpreted in terms of the benzene ring current.



12A



12B



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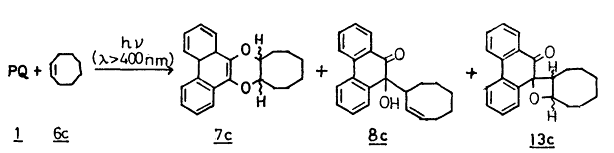
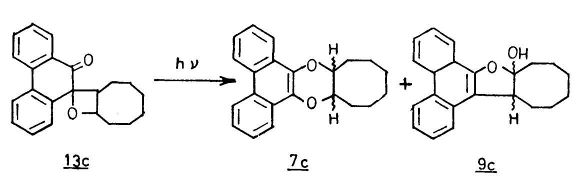
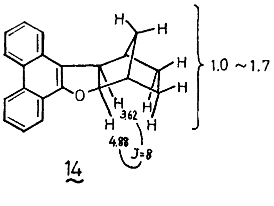
Photorearrangement of Oxetanes. Irradiation of a benzene solution of **1** with cyclooctene **6c** (300W high pressure Hg lamp) gave a mixture of **7c**, **8c**, and **9c** as described above. When the reaction was stopped at a relatively low conversion (irradiating light of a wavelength longer than 400nm), the corresponding oxetane **13** (18%) was isolated from the reaction mixture together with **7c** (39%, *cis*: *trans*=64: 36) and **8c** (5%). **9c** was not isolated. Further irradiation of **13c** dissolved in benzene using all the light of the high pressure lamp demostrated that **13c** easily photorearranged to **7c** and **9c** (relative ratio; 9 : 1). Since **7c** is photostable, the above results lead to the conclusion that **9a**—**d** and a part of **7a**—**d** are the photorearraged products of **13a**—**d**.





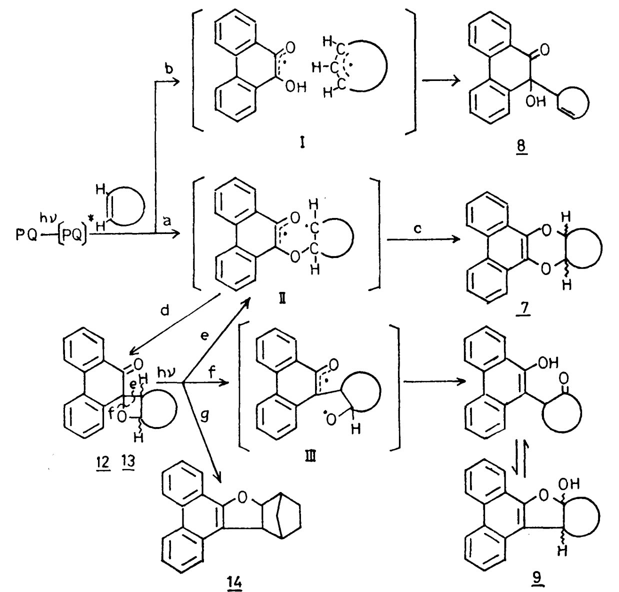


The oxetane **12** derived from norbornene, in comparison, was comparatively photostable, being ultimately decomposed under prolonged irradiation to give rather intractable products. After repeated column chromatography dihydrofuran **14** (*ca.* 12%) was isolated. On the basis of the ^1H-NMR spectrum the configuration of **14** was determined to be *exo*.[20]

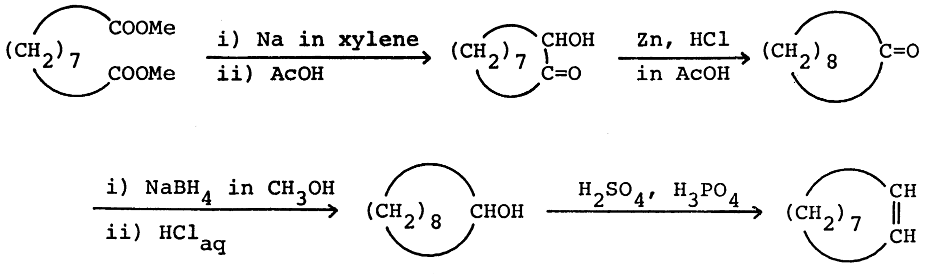
Discussion

Using cycloalkenes with a *cis*-configuration,[22] a mixture of the *cis*- and *trans*-dihydrodioxins were obtained in every reaction (Table 2). These results suggest that each of the dihydrodioxins was formed in a stepwise fashion, perhaps *via* a biradical intermediate. Similar experimental results have been reported in the reaction of **1** with *cis*-2-butane,[17] *trans*-2-butene,[17] and *trans*-stilbene.[18]

In the formation of oxetane the present investigation gives no unambiguous information. However, the results published strongly indicate the contribution of a biradical intermediate.[9,10] Possible reaction pathways compatible with the present results are shown in Scheme 1. Photoexcited phenanthrenequinone reacts with a olefin in two competitive manners; addition to the olefin to give II (path a) and hydrogen abstraction from the olefin resulting in the formation of a radical pair I (path b). As shown in Tables 1 and 2, cyclo-



Scheme 1.



Scheme 2.

octene is most reactive for path a and least for path b for the examined monocycloolefins, because the yield of **8** is least in this case. In addition, the resulting biradical II is likely to be of rather a longer lifetime compared with those derived from other monocycloolefins;[22] this has been deduced from the relatively high yield of the corresponding *trans*-dihydrodioxin, *i.e.*, *trans*-**7e**, since the *cis*- and *trans*-dihydrodioxins are photostable in general. Thus, the difference in energy barriers between path a and path b could be highest in the case of cyclooctene of the examined mono-cycloolefins. In the case of norbornene the difference is thought to be so large that path b can not contribute to the reaction, being coincident with the fact that the α-hydrogen atom to the double bond of norbornene corresponds to the bridge-head one. The difference in cycloolefin behavior may be attributed to the cumulative effect of the internal strain and the restricted freedom of the ring fluctuation (depending on the ring size).

The resulting biradical II is stablized to give **7** and **13** (or **12**). Further irradiation of **13** with the light from a high pressure Hg lamp gave two biradicals II and III, finally resulting in the formation of **7** and **9**. The relative preference of path c or path d was found to be strongly dependent on the structure of olefins. In the case of norbornene, path d was the exclusive course. In the case of cyclooctene there may be a comparatively high contribution of path d, since the highest yield of **9** was attained in the reaction. The high selectivity for path d in the cases of norbornene and cyclooctene is likely to be correlated with the lesser yield of **8** in the reactions. Although the mechanism still remains ambiguous, the relative preference for path d seems to be connected with the higher *s*-charactor of the relating orbitals in the ring closure, especially of the orbital in the olefin moiety. The special behavior of norbornene and other highly strained cycloolefins in photocycloadditions with 1,4-naphthoquinone have been reported by the present auther and co-workers.[21] The higher *s*-charactor of the relating orbitals will result in the stronger σ-bond and this may be the reason for the stable isolation of oxetanes **12** and **13** derived from norbornene and cyclooctene respectively. In the other cases, isolation of the corresponding oxetanes was unsuccessful, perhaps due to the lack of stability.

As described in the previous section, the oxetane **12** photochemically rearranges to hydroxydihydrofuran **9** and dihydrodioxin **7**. The photorearrangement of **12** to **9** is of novel type. Farid has isolated an oxetane in the reaction of phenanthrenequinone with 1,2-di-*t*-butylethylene. Investigation of the photorearrangement yielded a mixture of dihydrodioxin, furan, and dioxole. However, the hydroxydihydrofuran derivative has not been isolated.[19]

Experimental

Instrumentation. ^{1}H-NMR spectra were recorded with JEOL PS-100 spectrometer and chemical shifts have been recorded in δ units using tetramethylsilane as an internal standard. Infrared spectra were taken with a JASCO IR-G spectrometer. Ultraviolet and visible spectra were obtained with a Shimadzu UV-200 spectrometer. Mass spectra were recorded with a Hitachi M-52 mass spectrometer. Elemental analyses were performed at the Microanalysis Center of Kyoto University. VPC was carried out using a JEOL JGC-20K equipped with a flame ionization detector using a column of 5% Ucon oil LB 550X on 80—100 mesh Diasolid L. Melting points and boiling points of materials or products have not been corrected.

Materials. 9,10-Phenanthrenequinone (**1**) was prepared by the oxidation of phenanthrene[23]; mp 209—210 °C (lit, mp 208.5—210 °C). Cyclohexene (**6a**), cycloheptene (**6b**), *cis*-cyclooctene (**6c**), cyclododecene (**6g**), and bicyclo-[2.2.1]hept-2-ene (norbornene) (**11**) were commercially available (reagent grade) and used without further purification. Analyzed by VPC, cyclododecene (**6g**) proved to be a mixture of 30% *cis*- and 70% *trans*-isomer. Cyclononene (**6d**) was synthesized from diethyl azelate according to the route described above (Scheme 2); bp 160—172 °C (lit,[26] bp 167—169 °C/740 mmHg for the *cis*-isomer, 73—74 °C/30 mmHg for the *trans*-isomer); ^{1}H-NMR (CCl$_4$) δ 1.0—2.4 (14H, m), 5.56 (2H, m); IR (NaCl) 2910, 2840, 717, 728 cm^{-1}. Analysis by VPC and IR indicated that the synthesized cyclononene (**6d**) contained mainly the *cis*-isomer.

Cyclododecene (**6e**) and cycloundecene (**6f**) were synthesized from cyclodecanone and cycloundecanone, respectively. Cyclodecanone and cycloundecanone were synthesized from cyclododecanone in good yield by the method of Garbish and Wohlleke.[25] Cyclodecene (**6e**); bp 87—92 °C/42 mmHg (lit,[24] bp 194—195 °C/740 mmHg for the *cis*-isomer, 68—70 °C/10 mmHg for the *trans*-isomer); ^{1}H-NMR (CCl$_4$) δ 1.2—2.4 (16H, m), 5.48 (2H, m); IR (NaCl) 2900, 2840, 980 cm^{-1}. Analysis by VPC and IR indicated that the synthesized cyclodecene (**6e**) contained approximately 45% of the *cis*- and 55% of the *trans*-isomer. Cycloundecene (**6f**); bp 110—111 °C/40 mmHg; ^{1}H-NMR (CCl$_4$) δ 1.0—2.4 (18H, m), 5.30 (2H, m); IR (NaCl) 2905, 2840, 970 cm^{-1}. Analysis by VPC and IR indicated that the synthesized cycloundecene (**6f**) contained about 28% of the *cis*- and 72% of the *trans*-isomer.

*Irradiation of PQ (**1**) with Cycloalkene(**6a**—**g**) and Norbornene (**11**).* Pyrex test tubes were charged with PQ (**1**)

TABLE 4. ^{1}H-NMR SPECTRAL DATA OF PHOTOPRODUCTS (solv. CCl$_4$ or CDCl$_3$)

Compd	δ, ppm Ring proton	 Bridge-head methine proton	 Aromatic proton
7a	1.2—2.3 (8H, m)	3.48 (m) (2H) 4.08 (bd)	7.40 (4H, m) 8.04 (2H, m) 8.46 (2H, m)
7b	1.4—2.2 (10H, m)	3.70 (m) (2H) 4.25 (bd)	7.47 (4H, m) 8.16 (2H, m) 8.46 (2H, m)
7c	1.4—2.3 (12H, m)	4.00 (m) (2H) 4.41 (bd)	7.48 (4H, m) 8.12 (2H, m) 8.48 (2H, m)
7d	1.3—2.4 (14H, m)	4.20 (m) (2H) 4.56 (m)	7.50 (4H, m) 8.10 (2H, m) 8.54 (2H, m)
7e	1.4—2.4 (16H, m)	4.24 (m) (2H) 4.61 (m)	7.48 (4H, m) 8.08 (2H, m) 8.48 (2H, m)
7f	1.2—2.3 (18H, m)	4.22 (m) (2H) 4.56 (m)	7.60 (4H, m) 8.24 (2H, m) 8.64 (2H, m)
7g	1.2—2.1 (20H, m)	4.24 (m) (2H) 4.52 (m)	7.62 (4H, m) 8.26 (2H, m) 8.68 (2H, m)

Compd	δ, ppm Ring proton	 OH proton	 Olefinic proton	 Aromatic proton
8a	1.0—2.0 (6H, m) 2.3—2.5 (1H, m)	3.76 (s) 3.87 (s) (1H)	5.1—5.8 (2H, m)	7.2—8.0 (8H, m)
8b	1.0—2.6 (9H, m)	3.90 (s) 3.91 (s) (1H)	5.2—6.0 (2H, m)	7.2—8.1 (8H, m)
8c	1.0—2.9 (11H, m)	4.06 (1H, s)	5.1—5.7 (2H, m)	7.1—7.9 (8H, m)
8d	0.8—1.8 (12H, m) 2.6—2.9 (1H, m)	3.86 (1H, bs)	5.0—5.6 (2H, m)	7.1—8.0 (8H, m)
8e	0.8—2.0 (14H, m) 2.8—3.1 (1H, m)	3.84 (1H, s)	4.9—5.4 (2H, m)	7.2—8.0 (8H, m)
8f	0.8—2.8 (17H, m)	3.84 (1H, bs)	4.8—5.4 (2H, m)	7.0—8.0 (8H, m)
8g	0.8—2.8 (19H, m)	3.98 (1H, bs)	4.8—5.4 (2H, m)	7.0—8.0 (8H, m)

Compd	δ, ppm Ring proton	 OH proton	 Aromatic proton
9a	1.0—2.2 (6H, m) 2.2—2.6 (2H, m) 3.40 (1H, m)	broadened	7.60 (5H, m) 8.14 (1H, m) 8.66 (2H, m)
9b	1.0—2.6 (10H, m) 3.72 (1H, m)	2.80 (1H, bs)	7.64 (5H, m) 8.13 (1H, m) 8.72 (2H, m)
9c	1.1—2.1 (10H, m) 2.1—2.7 (2H, m) 3.26 (1H, m)	3.02 (1H, bs)	7.54 (5H, m) 8.10 (1H, m) 8.68 (2H, m)
9d[a]	1.2—3.4 (m) 3.60 (bd) 5.18 (bd)	3.08 (bs) 10.28 (s)	7.60 (m) 8.07 (m) 8.58 (m)
12	0.77 (2H, m) 1.08 (2H, d) 1.30 (1H, m) 1.78 (1H, bs) 2.42 (1H, d) 2.55 (2H, d) 4.80 (1H, d)	——	7.1—7.8 (8H, m)

a) Compound **9d** showed the complicated ^{1}H-NMR spectrum because hemiacetal ring was somewhat dissociated. Phenolic OH proton was observed at δ 10.28 ppm.

(1 mmol), cycloalkene (**6a—g**) (2 mmol) or norbornene (**11**) and reagent grade benzene (30 ml) (dried over sodium). The solutions were irradiated with a 300 W high-pressure mercury lamp and during irradiation, the test tubes were often shaken. The course of the reactions was followed by TLC. When the PQ had mostly disappeared the solvent was evaporated, and products separated by preparative silica gel TLC eluted with hexane–benzene or by florisil column chromatography eluted with hexane–benzene. The yield of products were determined from the weight of the corresponding fractions. The structures of each fraction were confirmed by means of ^{1}H-NMR technique. The crystalline products were recrystallized from hexane, benzene, or cyclohexane. The spectral data and the results of elemental analyses are summarized in Tables 4—6.

*Dehydration of **9c**, **9d**.* In a solution of hydroxydihydro-

TABLE 5. IR SPECTRAL DATA OF PHOTOPRODUCTS

Compd	ν, cm^{-1}		
	OH	C=O	C=C
7a			1620, 1600
7b			1620, 1600
7c			1620, 1600
7d			1620, 1600
7e			1620, 1600
7f			1620, 1600
7g			1625, 1600
8a	3450	1680	1600
8b	3450	1680	1600
8c	3470	1690	1600
8d	3470	1690	1600
8e	3450	1680	1600
8f	3450	1680	1600
8g	3450	1680	1600
9a	3400		1640, 1605
9b	3400		1640, 1605
9c	3400		1635, 1600
9d	3400		1640, 1605
12		1690	1600

TABLE 6. ELEMENTAL ANALYSES OF PHOTOPRODUCTS

Compd	Calcd					Found	
	Formula			(%)		(%)	
	C	H	O	C	H	C	H
7a	20	18	2	82.73	6.25		
7b	21	20	2	82.86	6.62	82.79	6.79
7c	22	22	2	82.98	6.96	82.97	7.19
7d	23	24	2	83.10	7.28	82.89	7.18
7e	24	26	2	83.20	7.56	83.32	7.67
7f	25	28	2	83.29	7.83	83.15	7.83
7g	26	30	2	83.38	8.07	83.45	8.09
8a	20	18	2	82.73	6.25	82.44	6.19
8b	21	20	2	82.86	6.62	82.85	6.62
9c	22	22	2	82.98	6.96	82.75	7.20
12	21	18	2	83.41	6.00	83.55	6.15

furane **9c,d** (20 mg) in methanol (20 ml), one drop of concd HCl was added. After standing for 1 h at room temperature, TLC analysis indicated that hydroxydihydrofurane (**9c**) had disappeared and furan (**10c**) exclusively formed. After evaporation of the solvent, product **10c** was recrystallized from pentane; mp 141—142 °C, which showed the following spectral data; ^{1}H-NMR (CCl_4) δ 1.2—2.1 (8H, m), 2.96, 3.10 (4H, two overlapped t), 7.50 (4H, m), 8.22 (2H, m), 8.61 (2H, m); IR (KBr) 1620, 1605, 1575 cm^{-1}; mass spcetrum *m/e* 300 (M$^+$). Found: C, 87.86; H, 6.51%. Calcd for $C_{22}H_{20}O$: C, 87.96; H, 6.71%.

Similarly, **10d** was obtained from **9d**. **10d**, mp 151.5—153 °C, gave the following spectral data; ^{1}H-NMR (CCl_4) δ 1.2—2.0 (14H, m), 2.92 (2H, t), 3.10 (2H, t), 7.42 (4H, m), 8.16 (2H, m), 8.52 (2H, m); IR (KBr) 1620, 1605, 1575 cm^{-1}; mass spectrum *m/e* 314 (M$^+$).

Irradiation through a Filter. A solution containing PQ (**1**) (216 mg, 1.04 mmol) and cyclooctene (**6c**) (219 mg, 1.99 mmol) in reagent grade benzene (30 ml) was irradiated with a 300W high-pressure mercury lamp through a filter (Toshiba color glass filter V-Y 42) to exclude light below 400 nm. After the usual work-up the products were separated by preparative TLC eluted with benzene. Products; dihydrodioxin (**7c**) (128 mg) (*cis*: *trans*=64:36), detectable amounts of α-hydrogen abstracted adduct **8c**, and oxetane **13c** (61 mg) were isolated. **13c**, mp 190—191 °C, slightly yellowish leaflets gave the following spectral data; ^{1}H-NMR ($CDCl_3$) δ 1.0—2.4 (12H, m), 2.88 (1H, ddd, J=2,8,8 Hz), 5.00 (1H, dd, J=8,14 Hz), 7.2—8.2 (8H, m); IR (KBr) 1680, 1600 cm^{-1}; UV λ_{max} ($CHCl_3$) 245 nm (ε 25000), 281 (2700), 327 (2900); mass spectrum *m/e* 318 (M$^+$). Found: C, 82.98; H, 6.96%. Calcd for $C_{22}H_{22}O_2$: C, 82.70; H, 6.72%. Under similar conditions, a benzene solution of PQ (**1**) with cyclododecene (**6g**) was irradiated, but no oxetane could be isolated.

*Photorearrangement of Oxetane **13c**.* A solution of oxetane **13c** (62 mg) in reagent grade benzene (10 ml) (dried over sodium) was irradiated with a 300W high-pressure mercury lamp for 25 h. The TLC analysis indicated that dihydrodioxin (**7c**) and hydroxydihydrofurane (**9c**) were formed. After evaporation of solvent, the residue was dissolved in methanol (10 ml) and one drop of concd HCl added. After standing for 1 h at room temperature, dihydrodioxin (**7c**) and furane (**9c**) were isolated after the usual work-up. The ratio of **6c** to **9c** was determined as 10:1 by means of ^{1}H-NMR spectroscopy utilizing the bridge-head methine protons of **6c** and methine protons adjecent to furane ring of **9c** as their indices.

*Photorearrangement of Oxetane **12**.* A solution of oxetane (**12**) (215 mg) in benzene (30 ml) was irradiated with a 300W high pressure Hg lamp for about 10 days. The TLC analysis indicated that oxetane (**12**) almost disappeared. After evaporation of the solvent, dihydrofurane (**14**) (24 mg) was isolated from the residue. The other products were an intractable matter. **14** was recrystallized from hexane, mp 136—138 °C, which gave the following spectral data; ^{1}H-NMR (CCl_4) δ 1.0—1.7 (6H, m), 2.66 (2H, bs), 3.62 (1H, d, J=8 Hz), 4.88 (1H, d, J=8 Hz), 7.40 (5H, m), 7.92 (1H, m), 8.48 (2H, m); IR (KBr) 1640, 1615 cm^{-1}; mass spectrum *m/e* 286(M$^+$). Found: C, 87.99; H, 6.22%. Calcd for $C_{21}H_{18}O$: C, 88.08; H, 6.34%.

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