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High Reactivity of Heterocoerdianthrones (HCDs) in Photoperoxidation and Thermal Stability of Their Endoperoxides. Use of HCD as a Photosensitizer under Sunlight

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The measured reactivity indices (β-values) of heterocoerdianthrones (HCDs) in self-sensitized photoperoxidation indicate a high reactivity toward singlet-oxygen. Such a high reactivity is not only due to an effective singlet-oxygen production due to the highly fluorescent character, but also due to a strained structure, as predicted by a molecular calculation. On the other hand, the large thermal stability of their endoperoxides (POs), revealed by the large activation energy in thermal decomposition, is also explained by considering the strained structure of the parent HCDs. As a prospect of solar synthesis, one of the HCD derivatives was applied to a photosensitizer for singlet-oxygen oxidation.

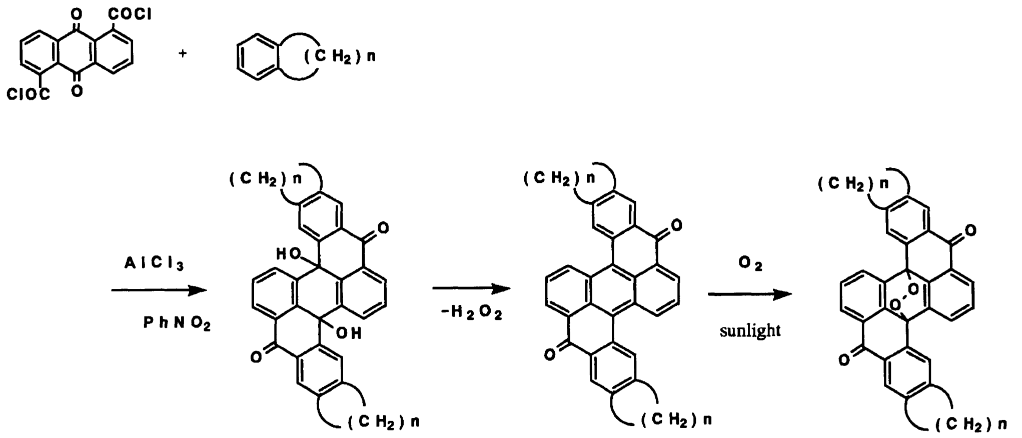
Heterocoerdianthrone (HCD) (**1a**), dibenzo[*a,j*]perylene-8,16-dione, is among the photochromic compounds, and was first synthesized by Scholl et al.[1] about sixty years ago. In an early experiment they observed the photoautooxidation of HCD under sunlight. Later, Dufraisse and Mellier[2] found that the photoautooxidation product of HCD was its endoperoxide (PO) (**2a**), which was converted reversively to HCD along with a release of oxygen. Recently, Brauer et al.[3—10] have paid attention to this photochromic compound and have continuously investigated the photochemistry of HCD. According to their investigation, HCD showed an extremely high reactivity toward singlet-oxygen, owing to its highly fluorescent character and effective production of singlet-oxygen in self-sensitized photooxidation.[3,4] Additionally, they reported a large thermal stability of PO,[3] and suggested the application of the HCD–PO system to a chemical actinometer.[10] The attractive properties of these compounds have prompted us to further study this class of compounds. In this paper we report on our study of the photo- and thermal chemistry of HCD derivatives and their endoperoxides.

Preparation of HCDs (1a—c) and Their Endoperoxides (2a—c). Since HCD (**1a**) was synthesized by Scholl et al.,[1] only a few methods for the preparation of **1a** and its derivatives have been reported.[11,12] In order to improve the synthetic availability, solubility toward organic solvents, and photo- and thermochemical properties of this useful photochromic compound, we attempted to prepare some HCD derivatives. Fortunately, its cycloalkylated derivatives (**1b** and **1c**) were obtained more easily from reactions of the acid chloride and indan or tetralin, respectively, when the reactants were treated under the Friedel–Crafts condition in the presence of aluminium chloride in nitrobenzene and the usual work-up was carried out. We assume that cyclization by twice aromatic electrophilic substitution to indan or tetralin and then an elimination of hydrogen peroxide from the adducts during work up were performed (Scheme 1). Thus, the obtained **1b** and **1c** exhibited the same electronic spectra as did **1a** (see Experimental), and showed a much better solubility than did **1a** toward several organic solvents.

As can been seen in self-sensitized photoperoxidation in **1a**,[4] when these newly prepared HCDs (**1b** and **c**) were irradiated under sunlight in benzene in the presence of oxygen, oxygen was added smoothly to give their endoperoxides (**2b** and **c**) in good yield along with a loss of the violet color of the HCDs.

Results and Discussion

Reactivity toward Singlet-Oxygen. The β-values (Table 1) obtained for HCDs (**1a**—**c**) by direct measurements of the relative quantum yields[13] in self-sensitized photooxidation (see Experimental) are of the order of 10^{-4} mol; these values indicate that HCDs are very reactive toward singlet-oxygen. Brauer et al.[3] reported the β-value of **1a** to be 6×10^{-4} mol in benzene, which was measured as a function of the dissolved oxygen concentration at 25°C. They established the mechanism of the self-sensitized photoperoxidation of **1a**, and explained its high reactivity in terms of the interaction of both the singlet and triplet states of HCD between molecular oxygen,[3] which effectively produces singlet-oxygen, and by a reencounter process[4] of ground state **1a** and singlet-oxygen to form the endoperoxide (**2a**). The β-value is regarded as being a reactivity index of the singlet-oxygen acceptor, and is generally related to the π-electron density of the acceptor, due to the electrophilic nature of singlet-oxygen. The β-values of HCDs measured by Brauer and us are considerably small, if HCDs are classified as being a quinone compound, and when the values are compared to the β-value, 4.5×10^{-2} mol,[14] of 9,10-diphenylanthracene (DPA), whose structure is involved in HCDs, since the electron density of the anthracene rings in the HCDs would be reduced due to the attached carbonyl groups.



1a, n=0
b, n=3
c, n=4

2a, n=0
b, n=3
c, n=4

Scheme 1.

Table 1. Reactivity Indices (β), Rate Constants (k) for Singlet Oxygen Addition of HCD (**1a**—**c**), and Activation Energies (E_a) for Thermal Decomposition of Endoperoxides (**2a**—**c**)

HCD	$\beta\times10^4$ a) / mol	$k\times10^{-8}$ b) / $mol^{-1}\,s^{-1}$	Endoperoxide	E_a c) / $kJ\,mol^{-1}$	log A
1a	1.16±0.15	3.61±0.47	**2a**	146.4±2.9	14.8±0.4
1b	0.82±0.06	5.06±0.37	**2b**	155.2±8.4	16.1±1.2
1c	0.97±0.19	4.28±0.84	**2c**	135.9±11.3	14.2±1.6

a) Estimated in Benzene at 25°C. b) Calculated from β-values using the life time 24 μs of singlet oxygen. c) Estimated from the decomposition rates of the endoperoxides in toluene at 80, 90, and 100°C.

The question is then raised as to why the HCDs have such high reactivities toward singlet-oxygen, even if one considers the highly fluorescent character of the HCDs.

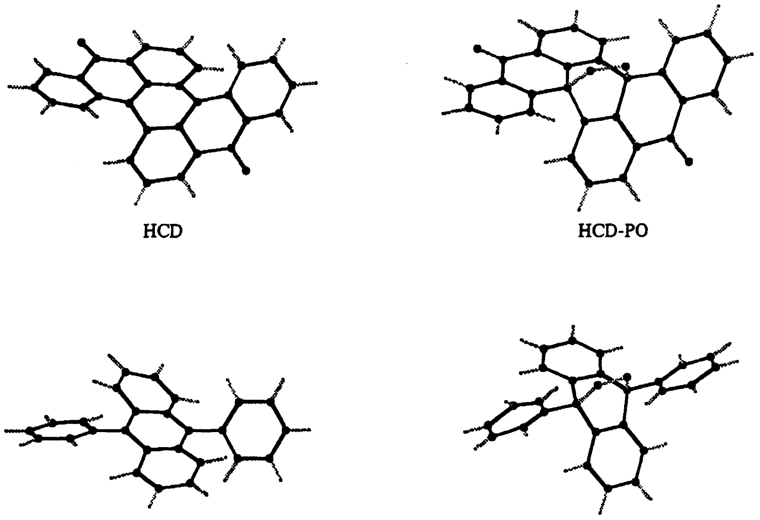
In order to compare the reactivity of HCD and DPA toward singlet-oxygen, molecular calculations were made, which considered only the interaction of the π-electrons of the acceptor and singlet-oxygen. The results of calculations by Hückel and *ab initio* SCF (STO-3G)[15] are given in Table 2. Both calculations predict the reaction sites correctly: That is, meso carbons (carbons of reaction sites) in the anthracene rings of HCD and DPA have the largest HOMO coefficients of all the aromatic carbons. However, the higher reactivity of HCD than DPA cannot be explained in terms of the calculated frontier electron densities of the reaction sites and the HOMO energies in consideration of the electrophilic nature of singlet-oxygen. Additionally, the superdelocalizabilities defined by Fukui et al.[16] as parameters of the reactivity of aromatic hydrocarbons toward electrophiles were also applied in order to compare the reactivities of HCD and DPA. The superdelocalizability of HCD is calculated as being 1.744, which is much smaller than the value of 2.638 for DPA and, yet is smaller than the reported value of 1.989 for naphthalene,[16] which does not react with singlet-oxygen. By considering only these results, HCD would not be as reactive toward singlet-oxygen as expected from the β-value. Of course, these calculations are too simple and do not correctly reflect the other factors, which are characteristic for HCDs, but, conversely, suggest the importance of other factors.

Interestingly, energy minimization by MM2 for the molecular orbital calculation gives a stereo view of HCD, DPA, their endoperoxides HCD–PO and DPA–PO, as illustrated in Fig. 1. The illustration shows that two phenyl groups of DPA which attach to the anthracene ring are twisted by ca. 60° against the anthracene plane by a steric hindrance of hydrogen atoms (this is well-established fact),[17] and that two anthrone moieties of HCD and HCD–PO are twisted by about 26° and 60°, respectively. These structural views permit us to speculate that the anthracene ring of HCD would be considerably strained, since the HCD molecule is constructed by tying twisted phenyl groups to the anthracene ring of DPA through the carbonyl groups; also, the carbon framework of HCD is somewhat structurally close to its endoperoxide. The unusual reactivities of highly strained aromatics toward singlet-oxygen were reported by Wasserman and Keehn,[18] as well as Gray and Boekelheide,[19] respectively, where strained

Table 2. Molecular Calculation of HCD, DPA and Their Endoperoxides

		HCD	HCD–PO	DPA	DPA–PO
Frontier electron density of reaction site (Hückel)		0.2543		0.2946	
HOMO energy[a)]	Hückel (λ)	0.5480		0.3111	
	STO-3G (u)	−0.1870		−0.1647	
Total energy	STO-3G (u)	−1203.0466	−1350.8149	−982.9344	−1130.5185

a) HMO energies were described with λ in Hückel MO calculation and with atomic unit in STO-3G.


HCD

HCD-PO

DPA

DPA-PO

Fig. 1. Stereo view of HCD, DPA, and their endoperoxides illusarated by MM2 Minimization.

benzene or naphthalene rings were converted by sensitized photooxidation to give endoperoxides as the initial products. These strain effects on the reactivity can also be applied to HCD. In order to explore the assumption that the twisted structure of HCD should produce a high strain energy in this molecule and exhibit high reactivity, the total energy deferences in reactions of singlet-oxygen with HCD and DPA were calculated by *ab initio* SCF (Hartree–Fock) (Table 2). The deference between (HCD+singlet-oxygen)[20)] and the endoperoxide (HCD–PO) was calculated as 0.2968 u (atomic unit). On the other hand, the deference between (DPA+singlet-oxygen) and its endoperoxide (DPA–PO) was obtained as 0.1126 u. Although these values exhibit only qualitative meaning, the larger deference in HCD than in DPA is clear, and this large deference indicates a much higher energy in the HCD molecule, and should be ascribed to the strain energy. This strained framework of HCD reasonably explains its high reactivity. Brauer et al.[20)] found that benzo[1,2,3-*kl*: 4,5,6-*k′l′*]dixanthene, which is structurally close to HCD and should thus be strained, was very reactive in photoperoxidation, where the rate constant was 8.2×10^{7} mol^{-1} s^{-1}. However, they did not mention the relationship between the structure and reactivity. This observation of theirs strongly supports the reactivity of a strained anthracene ring in HCD. Thus, the predicted strain of HCD also reflects the large thermal stability of endoperoxides **2a**—**c**, as discussed in the following section.

Thermal Stability of Endoperoxides of HCDs. It is well-established that DPA endoperoxide decomposes to DPA and singlet-oxygen[21)] and that the photolysis of **2a** gives the parent HCD and singlet-oxygen;[6)] however, whether singlet-oxygen is truly formed in the thermal decomposition of HCD endoperoxide has not yet been described to our knowledge.

When the endoperoxide (**2c**) was heated in benzene under reflux for 29 h in the presence of α-terpinene (α-terpinene/endoperoxide=5/1), ascaridol, endoperoxide of α-terpinene, was obtained in 5% yield, based on **2c**. Considering the long half-life ($t_{1/2}$=120 h) of **2c** at 80°C, the conversion of the endoperoxide was calculated to be 16%. Thus, the yield of ascaridol was estimated to be ca. 31%. This result clearly indicates the formation of singlet-oxygen in the thermal decomposition of **2c**.

As shown in Table 1, large activation energies of **2a**—**c** exhibit an extreme thermal stability, compared to other anthracene endoperoxides; for instance, 116.3

kJ mol^{-1} is known for DPA endoperoxide.[21] These large activation energies of HCD endoperoxides also mean that the parent anthracene ring in HCDs should have a large ring strain, as pointed out by Wasserman and Larsen[23] regarding the polymethylated naphthalene system. They showed the relationship between the activation energies of endoperoxides and the imaginary strains of the parent polymethylated naphthalenes; namely, the more strain that the parent methylated naphthalene has, the greater is the increase in the activation energy of its endoperoxide during thermal decomposition to form the parent naphthalene. By applying this matter to HCDs, the ring strain predicted in the previous section explains the thermal stabilities of the endoperoxides of the HCDs

Use of HCD (1c) as a Photosensitizer. As can be seen in the self-sensitized photoperoxidation of HCDs, they would be good energy-transfer materials as sensitizers for singlet-oxygen production under natural sunlight. In spite of the high reactivity of HCDs toward singlet-oxygen, the possibility of their use for solar synthesis is expected. We thus attempted the capture of singlet-oxygen formed during self-sensitized photoperoxidation of HCDs under natural sunlight in the presence of organic singlet-oxygen acceptors.

When a benzene solution of α-terpinene and **1c** was stirred at room temperature under an oxygen atmosphere and sunlight, the red-violet color of **1c** gradually became bleached, and α-terpinene was oxidized to ascaridol. This oxidation was also effective under an aerobic atmosphere. Examples employing other unsaturated compounds as singlet-oxygen acceptors are listed in Table 3. Depending on the structures of the used unsaturated compounds, both the ene and Diels–Alder type reactions which are characteristic of singlet-oxygen oxidation[24] were observed. These oxidations, of course, essentially compete with the self-sensitized peroxidation of **1c**, and the relative reactivity of the reactants reflects the yields of the oxidation products. By making a comparison with tetraphenylporphine (TPP), known as a typical photo-sensitizer, **1c** was found to be almost as effective as TPP under the same conditions. This oxidation using the HCD derivative as a photosensitizer is one example of a solar synthesis which is simple and does not require any special equipment.

Experimental

The melting points were determined with a Yanagimoto hot-stage apparatus and are uncorrected. Microanalyses were performed on a Perkin–Elmer PE 2400 CHN elemental analyzer. IR spectra were recorded on a JASCO IRA-1 spectrometer, ^{1}H NMR spectra on a JEOL PMX 60 (60 MHz), and mass spectra on a JEOL JMS-01SG-2 spectrometer. Absorption spectra were measured with a Shimadzu UV-3100 spectro-photometer.

Preparation of HCD (1a—c) and Their Endoperoxides (2a—c). HCD (**1a**) and its endoperoxide (**2a**) were synthesized according to a method of Scholl et al.[1] and purified by column chromatography before use.

1,2,3,10,11,12-Hexahydrodiindeno[5,6-*a*: 5′,6′-*j*]-perylene-8,17-dione (1b). To an ice-cooled solution of anthraquinone-1,5-dicarbonyl dichloride (13.5 g, 0.041 mol) in nitrobenzene (90 ml) was added aluminium chloride (33 g, 0.25 mol) and indan (25 ml, 0.2 mol). The reaction mixture was stirred for 2 h at 0°C and for 2 d at room temperature. After the addition of ice water (100 ml), the solvents and unreacted reactants were removed by steam distillation. The residue was filtered and washed with 12% aqueous ammonia and water until the filtrate became neutral. The product was dried in vacuo (17.2 g, 91% based on acid chloride) and recrystallized from chloroform: IR (KBr) 1640 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.9 (4H, m, $CH_2C\underline{H}_2CH_2$), 2.73—3.23 (8H, m, $C\underline{H}_2CH_2C\underline{H}_2$), 7.23—7.77 (4H, m, H-5, 6, 14, and 15), 8.06 (2H, s, H-4, and 13), 8.27—8.73 (4H, m, H-7, 9, 16, and 18); MS, m/z 462 (M^+). Found: C, 87.82; H, 4.35%. Calcd for $C_{34}H_{22}O_2$: C, 88.29; H, 4.79%.

1,2,3,4,11,12,13,14-Octahydrodinaphtho[2,3-*a*: 2′,3′-*j*]-perylene-9,19-dione (1c) was synthesized in the same way as described above using tetralin instead of indan in 23% yield: Mp 328°C; IR (KBr) 1640(C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.5—2.13 (8H, m, $CH_2C\underline{H}_2C\underline{H}_2CH_2$), 2.5—3.1 (8H, m, $C\underline{H}_2CH_2CH_2C\underline{H}_2$), 7.23—7.77 (4H, m, H-6, 7, 16, and 17), 8.03 (2H, s, H-5 and 15), 8.3—8.87 (4H, m, H-8, 10, 18, and 20); Ms, m/z 490 (M^+). Found: C, 88.10; H, 5.54%. Calcd for $C_{36}H_{26}O_2$: C, 88.13; H, 5.34%.

The UV spectral data of **1a**—**c** are listed in Table 4.

1,2,3,4b,10,11,12,13b-Octahydro-4b,13b-(epidioxy)-diindeno[5,6-*a*: 5′,6′-*j*]perylene-8,17-dione (2b). A suspension of HCD (**1b**) (0.2 g, 0.408 mmol) in benzene (60 ml) was irradiated by sunlight under an aerobic atmosphere until the violet color was disappeared. The solvent was then evaporated and the residue chromatographed (SiO_2, chloroform as a eluant) to give **2b** (0.17 g, 85%); ^{1}H NMR ($CDCl_3$) δ=2.22 (4H, q, J=8 Hz, $CH_2C\underline{H}_2CH_2$), 3.1 (8H, t, J=8 H, $C\underline{H}_2CH_2C\underline{H}_2$), 7.2—7.4 (4H, m, H-5, 6, 14, and 15), 7.66 (2H, m, H-4 and 13), 7.93—8.2 (2H, m, H-7 and 16), 8.33 (2H, s, H-9 and 18); Ms m/z 494 (M^+). Found: C, 82.35; H, 4.13%. Calcd for $C_{34}H_{22}O_4$: C, 82.57; H, 4.48%.

1,2,3,4,5b,11,12,13,14,15b-Decahydro-5b,15b-(epidioxy)dinaphtho[2,3-*a*: 2′,3′-*j*]perylene-9-19-dione (2c) was prepared by the same way in 21% yield; ^{1}H NMR ($CDCl_3$) δ=1.63—2.3 (8H, m, $CH_2C\underline{H}_2C\underline{H}_2CH_2$), 2.63—3.2 (8H, m, $C\underline{H}_2CH_2CH_2C\underline{H}_2$), 7.07—7.43 (4H, m, H-6, 7, 16, and 17), 7.53 (2H, s, H-5 and 15), 7.9—8.27 (2H, m, H-8 and 18), 8.18 (2H, s, H-10 and 20); MS m/z 522 (M^+). Found: C, 82.62; H, 5.27%. Calcd for $C_{34}H_{22}O_4$: C, 82.47; H, 5.02%.

Measurement of β-Values. The β-values of HCDs (**1a**—**c**) were estimated directly from measurements of the relative quantum yields of HCD's consumption using a form of the following equation:[13]

$$1/[\mathrm{POs}] = 1/\left(I_{\mathrm{abs}}\phi_{\mathrm{isc}}\right)\left(1+\beta/[\mathrm{HCDs}]\right),$$

where [HCDs] and [POs] are the concentrations of HCDs and endoperoxides, respectively, as determined by monitoring the decrease in the absorbance of HCDs; I_{abs} is the number of mole quanta per liter absorbed during the irradiation time, ϕ_{isc} is the intersystem-crossing quantum yield for the

Table 3. Photoperoxidation of Alkenes Using **1c** as a Photosensitizer a)

Reactant	Molar ratio Reactant/**1c**	Solvent	Reaction time b) h	Product c)	Yield d) %
α-Terpinene	9	Benzene	0.5	Ascaridole	81
	20	Benzene	1.5		77
	80	Benzene	5.0		59
1,3-Cyclohexadiene	10	Benzene	3.5	5,6-Dioxabicyclo-[2.2.2]octene-2	9
	100	Benzene	8		36
Cyclopentadiene	100	CCl_4	2.5	4,5-Epoxy-cis-2-pentenal	21
	100 e)	CCl_4	2.5		23
2,3-Dimethyl-2-butene	100	CCl_4	3	3-Hydroperoxy-2,3-dimethyl-1-butene	40
	100 e)	CCl_4	3		47

a) All reactions were carried out by irradiation of sunlight under oxygen atmosphere. b) The reaction times are that needed until the color of **1c** disappeared. c) Purified by kugel rohr distillation. d) Yields are based on reactants. e) TPP (tetraphenylporphine) was used as a photosensitizer instead of **1c**.

Table 4. UV Spectra of Prepared HCDs (**1a**—**c**) a)

	λ_{max}/nm	ε
1a	574 (573)	28256 (26562)
1b	589 (589)	22805 (21405)
1c	587 (587)	20235 (17553)

a) Measured in benzene and the data in parentheses are values measured in toluene.

sensitizer, and β is the ratio of the decay rate of singlet oxygen to the rate of its reaction with the acceptor. These β-values were estimated to be the ratio of the slope to the intercept on the 1/[POs] axis, which were obtained from plots of 1/[POs] vs. 1/[HCDs]. To this end, each solution of four or five different concentrations of HCDs (**1a**—**c**) (for **1a**; 0.13, 0.26, 0.53, and 1.04×10^{-4} mol dm^{-3}, **1b**; 0.29, 0.38, 0.61, 0.94, and 1.50×10^{-4} mol dm^{-3}, **1c**; 0.50, 0.66, 0.84, 1.02, and 1.34×10^{-4} mol dm^{-3}) in oxygen-saturated benzene was irradiated by a high-pressure Hg arc through a Toshiba-43 filter for 8 min. (**1a** and **1b**) and for 16 min. (**1c**) at 25°C, all in a same geometry. The [HCDs] and [POs] were determined by quantitative UV spectroscopy at each λ_{max} of HCDs assuming that all of the HCDs decrease was equal to the increase of the POs. The addition rates (k) were calculated from the equation $k=(\beta\tau)^{-1}$, where τ (=24 μs) is the lifetime of singlet-oxygen in benzene at 25°C, as determined by Merkel and Kearns.25)

The results are listed in Table 1.

Measurement of the Activation Energy in the Thermal Decomposition of Endoperoxides. Solutions of endoperoxides (**2a**—**c**) were prepared by the irradiation of the HCDs (**1a**—**c**) solution in toluene (1.5×10^{-4} mol dm^{-3}) under sunlight and an oxygen atmosphere until the violet color of the HCDs disappeared. These solutions were heated at 80, 90, and 100°C by an oil bath having a temperature-control equipment in order to decompose to oxygen and parent HCDs. The increase of HCDs was monitored by quantitative UV spectroscopy at every 90 min for 80°C, 60 min for 90°C and 100°C. Plots of $-\ln$ [POs] (calculated from the relationship $[\text{POs}]=[\text{POs}]_0-[\text{HCDs}]$) vs. time give straight lines, the slopes of which are the decomposition rates (k'). The activation energies and log A were estimated from the slopes and intercepts obtained by plotting ln k' vs. the reciprocal of K (reaction temperature). The data are listed in Table 1.

Use of HCD (1c) as a Photosensitizer. Ascaridole: A solution of HCD (**1c**) (0.04 g, 8.16×10^{-5} mol) and α-terpinene (0.1 g, 7.35×10^{-4} mol) in benzene (20 ml) was irradiated by sunlight under an oxygen atmosphere at ambient temperature with stirring until the violet color of **1c** disappeared (0.5 h). After evaporation of benzene, the residual oil was distilled by kuhgel rohr (oven temperature 100°C at 53 Pa) to give pure ascaridole (0.10 g, 81%): ^{1}H NMR (CCl_4) δ=1.00 (6H, d, J=6 Hz, CH_3), 1.27 (3H, s, CH_3), 1.50—2.30 (5H, m, CH_2CH_2 and CH), 6.30 (2H, s, CH=CH).26a)

In a similar manner, other oxidation products were obtained; the ratios of the singlet-oxygen acceptors to the sensitizer (**1c**) are listed in Table 3. The following ^{1}H NMR data are in good agreement with those reported.

5,6-Dioxabicyclo[2.2.2]octene-2:26b) Bp 110°C (oven temperature at 6.7 Pa); ^{1}H NMR (CCl_4) δ=1.20—1.97 (2H, m, *endo*-CH_2CH_2), 2.00—2.87 (2H, m, *exo*-CH_2CH_2), 4.50 (2H, brs, CH), 6.57 (2H, m, CH=CH).

4,5-Epoxy-*cis*-pentanal:26c) Bp 90°C (oven temperature at 400 Pa); ^{1}H NMR (CCl_4) δ=2.45—2.83 (1H, m, $C\underline{H}$=CHCHO), 2.83—3.20 (1H, m, CH=$C\underline{H}$CHO), 4.00—4.06 (1H, m, $C\underline{H}$CH=CHCHO), 5.73—6.33 (2H, m, $OC\underline{H_2}$-CHCH=CHCHO), 9.83—10.01 (1H, m, CHO).

3-Hydroperoxy-2,3-dimethyl-1-butene:26b) Bp 55°C (oven temperature at 1560 Pa); ^{1}H NMR (CCl_4) δ= 1.30 (6H, s, $(CH_3)_2COO$), 1.78 (3H, d, J=1 Hz, CH_3C=C), 4.92 (2H, m, C=CH_2), 8.38 (1H, brs, OOH).

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