

Photoproduct Distribution Spectrum of the Sensitized Photoreaction of 1,4-*p*-Benzenonaphthalene

Masaru Kimura,* Katsumi Nukada, Kyosuke Satake, and Shiro Morosawa

Department of Chemistry, Faculty of Science, Okayama University, Tsushimanaka 3-1-1, Okayama 700, Japan

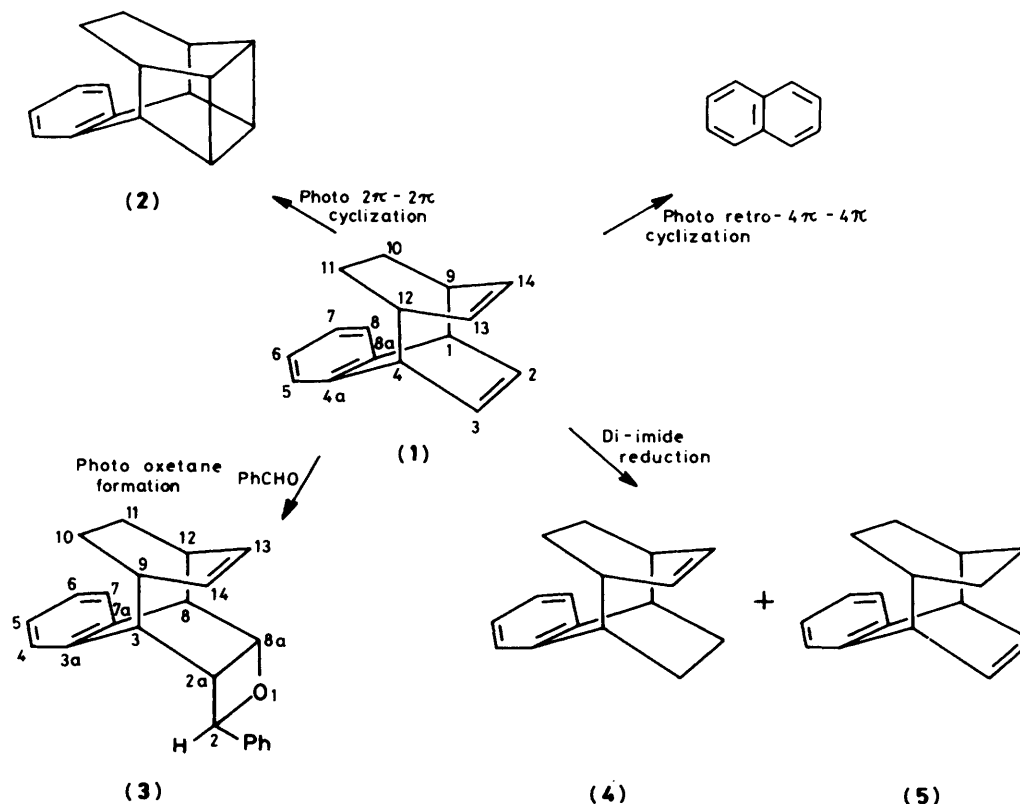
A correlation between the type of the photoproducts of 1,4,9,10,11,12-hexahydro-1,4-*p*-benzenonaphthalene (1) and triplet carbonyl and non-carbonyl sensitizers has been investigated. Electron transfer from the alkene moiety of (1) to excited sensitizers may cause the formation of naphthalene. The cage compound (2) was formed *via* energy transfer from excited sensitizers ($E_t \geq 71$ kcal/mol) to the triplet state (T_1) of (1). The irradiation of benzaldehyde and (1) gave the cage compound (2) and (2*RS*, 2*aRS*, 3*SR*, 9*RS*)-2*a*,3,8,8*a*,9,10,11,12-octahydro-3,8-*p*-benzeno-2*H*-naphth[2,3-*b*]oxete (3).

From the pattern set by the intermolecular cycloaddition of alkenes, we expected that when structural constraints favour cycloaddition, intramolecular cycloadditions should occur with high efficiency.¹ An example of this is the efficient intramolecular photocycloaddition of norbornadiene, induced by both direct² and photosensitized excitation,³ to form quadricyclane. Although this system has been discussed in terms of nonvertical energy transfer,^{1,3} it has been noted that since the quadricyclane–norbornadiene interconversion involves a strong interaction with the excited singlet state of the sensitizers used, triplet energy transfer may not be involved.⁴ We have investigated this system further using the 1,4-*p*-benzeno-

isomerization of (1); (b) benzaldehyde quenches the excited state by causing $[2\pi + 2\pi]$ cycloaddition of the diene (1) to the aldehyde; and (c) naphthalene is formed as a result of $[4\pi + 4\pi]$ cycloreversion by photochemical electron-transfer or by electrochemical oxidation of (1).

Results and Discussion

Sensitized irradiation of a benzene solution of (1) with benzaldehyde under an argon atmosphere gave the *p*-benzenonaphth[2,3-*b*]oxete (3),^{6,†} the cage compound (2), and naphthalene. The structural assignment of (3) was based on the



naphthalene (1), a compound having the strongest interacting nonconjugated π system known,⁵ and found that the photoproduct distribution clearly depends on the triplet energy of the sensitizers. We now report that (a) benzaldehyde and other triplet sensitizers sensitize the intramolecular $[2\pi + 2\pi]$ cyclo-

† Although an interesting example of the addition of benzophenone in the n,π^* triplet state to a σ -bond in quadricyclane is known,⁶ the irradiation of the benzene solution of (1) (15 mM) and benzaldehyde (0.75 M) with a 450 W high-pressure mercury lamp through a Pyrex filter under a nitrogen atmosphere failed to give the corresponding oxetanes.

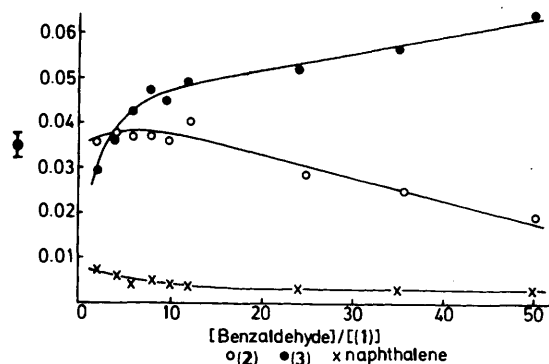


Figure 1. The quantum yields (Φ) for the formation of naphthalene, (2), and (3) in benzene as a function of the ratio of $[\text{benzaldehyde}]/[(1)]$. Concentration of (1) is 0.025M in each sample.

following spectral properties. Absorption at 965 cm^{-1} in its i.r. (Nujol) spectrum indicates the presence of the oxetane ring. ^1H N.m.r. resonances for olefinic protons at δ 6.13 coupled with methine protons at *ca.* δ 2.75 (9-H, 12-H) whose resonances appear upfield of the other doublet methine protons at δ 3.37 (3-H, 8-H) adjacent to the benzene ring of (3). This result shows that the double bond closer to the benzene ring in (1) was selectively attacked by benzaldehyde. Since the di-imide reduction of (1) gave the corresponding dihydro compound (4) as the main product which was formed by the attack of di-imide from the less hindered side of (1),⁷ the selective formation of (3) may be explained similarly. The coupling constant $J_{2,2a} = 5\text{ Hz}$ allows the stereochemistry of the phenyl group on the oxetane ring to be assigned reasonably as *exo*.

Quantum yields for formation of naphthalene, cage compound (2), and the naphthoxete (3) were determined with a degassed benzene solution of (1) (15 mm) and benzaldehyde at various concentrations (Figure 1). An increase in benzaldehyde concentration gives an increase in the quantum yield of naphthoxete formation, little change in the formation of naphthalene, and a decrease in the formation of (2). The sum of the quantum yields for formation of (2) and (3) is almost constant when the ratio is $>10:1$ for the concentration of benzaldehyde: (1); at this ratio the aldehyde absorbs more than 90% of incident light. The dependence of benzaldehyde concentration on the formation of the naphthoxete (3) may be explained in terms of $[\text{benzaldehyde}:(1)]^*$ exciplex formation, higher concentrations of the aldehyde giving rise to the formation of (3). However, cleavage of the exciplex results in triplet energy transfer to (1). Stern-Volmer plots for the formation of the naphthoxete and naphthalene in the photoreaction of (1) in the presence of benzaldehyde shows that formation of the naphthoxete (3) and the cage compound (2) were quenched with cyclohexa-1,3-diene. The lifetimes of the triplet intermediates for these products are calculated to be the same within experimental error ($4.5 \times 10^{-9}\text{ s}$),* and we assume that the intermediates are identical. The product distribution was not related to secondary reactions (see Table 1).

We summarize the correlation between the type of photoproducts and the triplet energy of carbonyl and non-carbonyl sensitizers in the photosensitized reaction of (1) as follows. (1) Naphthalene formation was observed from the direct irradiation and the sensitized reactions using both higher-energy sensitizers ($E_t \approx 80\text{ kcal/mol}$) and lower-energy sensi-

Table 1. Time dependency on product distribution of the photoreaction of (1) in the presence of benzaldehyde^a

Reaction time (h)	Product Yield (%)		
	Naphthalene	(2)	(3)
2	6.7	49.4	43.9
4	6.3	47.0	46.7
6	6.0	48.0	46.0

^a Compound (1) (0.025M) and benzaldehyde (0.15M) in benzene (4 ml).

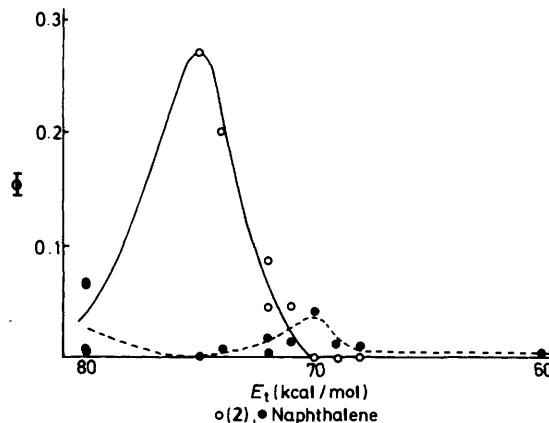


Figure 2. The photoproduct distribution spectrum of the sensitized photoreaction of (1) versus the triplet energy of carbonyl and non-carbonyl sensitizers.

tizers (around $E_t = 71\text{ kcal/mol}$). The relatively high yield of naphthalene formation, however, may be caused by a singlet sensitized reaction by naphthalene-2-carbaldehyde.† It was found that acetophenone, xanthone, benzaldehyde, and 4-methoxyacetophenone, sensitizers whose triplet states are between 80 and 71 kcal/mol, are extremely efficient for the formation of (2). (3) The crossing point at 71 kcal/mol in Figure 2 is reasonably assigned to the lower excited triplet state (T_1) of (1).‡ (4) Using benzophenone and dicyanobenzene, an inefficient sensitizer for the energy transfer to (1) whose triplet energies are lower than the T_1 of (1), only naphthalene was observed.

Since naphthalene was the major product from the direct irradiation (see Table 2), we needed to confirm whether such sensitized reactions occurred where there was complete light absorption by the sensitizers. Judging from the quantum yields for the formation of naphthalene in Table 1, direct photo-absorption by (1) contributes little to naphthalene formation.§ An electron transfer process may be involved in these

† One of the present authors has pointed out the possibility of exciplex formation between the n,π^* singlet state of naphthalene-2-carbaldehyde and olefins. Therefore, we assume that the singlet exciplex [naphthalene: (1)]* gives naphthalene. (N. C. Yang, M. Kimura, and W. Eisenhardt, *J. Am. Chem. Soc.*, 1973, **95**, 5058).

‡ Judging from the energy of the first excited state of norbornadiene at 72 kcal/mol,¹⁴ 71 kcal/mol is a reasonably acceptable value for that of the first triplet state of (1) which has a similar system to norbornadiene.

§ When the ratio of absorption coefficients for benzaldehyde and (1) is higher than 25:1, we considered that the contribution for the quantum yield of the formation of naphthalene by the direct irradiation of (1) would be negligible. The concentrations of all other sensitizers in Table 1 satisfied the above requirement.

* The lifetimes were calculated from the slopes (K_q) of Stern-Volmer plots for the formation of (2) and (3) with cyclohexadiene as a quencher using $K_q = 5 \times 10^9\text{ M s}^{-1}$ in benzene.⁸

Table 2. Correlation between the type of the photoproducts and the triplet energy (E_t) of carbonyl and non-carbonyl sensitizers in the photosensitized reaction of (1)

Sensitizer conc. (M)	Absorption coefficient ϵ at 3 130, 2 537 Å	E_t (kcal/mol) ¹⁰	Relative yield of products (%)			Φ^a
			Naphthalene	(2)	(3)	
9,10-Dibromoanthracene ^{5a} (0.005)		40	Trace			
2,3-Benzophenanthrene ^{5a} (0.005)		50	Trace			
Benzoquinone ^{5a} (0.005)		50	Trace			
Benzil (0.025)	500	55	Trace			
Naphthalene-2-carbaldehyde (0.005)	1 200	59	100			0.017
α -Naphthoquinone (0.005)	1 950	60	Trace			
Fluorene (solvent)	20	68	100			0.009
Benzophenone (0.255)	50	69	100			0.012
1,4-Dicyanobenzene (solvent)	2 500	70	100			0.04
4-Methoxyacetophenone (0.005)	1 700	71	23	77		0.06
4-Chloroacetophenone (0.231)	47	72	26	74		0.06
Benzaldehyde (0.25)	20	72				
(0.25)*			4	60	36	0.085
Xanthone (0.045)	3 000	74	10	49	41	0.13
Acetophenone (0.045)	4 000	75	3	97		0.218
Acetone (solvent)	3	80		100		0.269
1,4-Dichlorobenzene ^b (solvent)	120	80	54	46		0.132
(1)† (0.045)	8 660	77	47	53		0.01
			100			0.046

* In this case, the photoreaction was carried out in acetonitrile. † The direct irradiation at 2 537 Å was a performed by a 450 W Ushio high-pressure lamp through an appropriate filter system (see Experimental section). ^a Quantum yield for photoproduct formation. ^b These sensitized irradiations were performed with same light source and filter system as that used in the direct irradiation of (1).

sensitized photoreactions of (1), a retro[4 π + 4 π]cycloaddition by an electron transfer mechanism having been observed in the photosensitized reaction of the anthracene dimer, a compound which has a similar structure to that of (1).⁹ The likelihood of such a process was supported by the higher quantum yield obtained when *p*-dicyanobenzene was used as sensitizer (triplet energy almost the same as that of benzophenone), and by the electrolysis of (1) to give naphthalene in good yield. Use of a sensitizer with an E_t value just below that of T_1 gave the most efficient electron transfer. It is interesting that this photo-system should bring about energy transfer and electron transfer reactions with such sensitizers, and in this connection we should like to note that the arrangement of chromophores with through-bond overlap in (1) may make it a good electron donor and an energy acceptor.

Experimental

All m.p.s are uncorrected. I.r. spectra were obtained on a JASCO IRA-1 spectrometer. U.v. spectra were measured with a Hitachi UV-200 spectrometer. ¹H N.m.r. spectra were recorded on a JEOL-JNM-PX60 spectrometer (60 MHz) with tetramethylsilane as an internal standard. G.l.c. analyses were performed on a YANACO G-180 gas chromatograph (5% OV-17 Chamelite CK 80/60 column, 1.5 × 5 mm).

(2RS,2aRS,3SR,9RS)-2a,3,8,8a,9,10,11,12-Octahydro-3,8-*p*-benzeno-2H-naphth[2,3-*b*]oxete (3).—A solution of the benzenonaphthalene (1) (417 mg, 2 mmol) and benzaldehyde (106 mg, 1 mmol) in dry benzene (110 ml) was irradiated with a Ushio 450 W high-pressure mercury lamp through a Pyrex filter for 5 h under an argon atmosphere. The solvent was then removed under reduced pressure and the residue chromatographed on silica gel eluting with (hexane-EtOAc 10:1) to give (3) (132 mg, 42%),⁶ cage compound (2) (106 mg, 25%; m.p. 90–91 °C⁵), and naphthalene (13 mg, 5%). Compound (3) had m.p. 112–113 °C; $\delta_{\text{H}}(\text{CCl}_4)$ 1.33 (4 H, m), 2.50–3.00 (2 H, m, $J_{9,3} = J_{12,8} = 12$ Hz), 3.11 (1 H, sext, $J_{2a,3} 4$ Hz, $J_{2a,8a} 7$ Hz, $J_{2a,2} 5$ Hz), 5.30 (1 H, q, $J_{8a,2a} 7$ Hz, $J_{8a,8} 4$ Hz), 6.13 (2 H, m, pseudo A_2B_2), and 7.13 (4 H, ArH); $\nu_{\text{max.}}$ (Nujol) 1 583, 965, 812, 755, and 724 cm^{-1} ; $\lambda_{\text{max.}}$ (EtOH) 274 (ϵ 497), 266 (682), 260 (712), 253 (718), and 203 nm (34 300) (Found: C, 87.45; H, 7.0. Calc. for $\text{C}_{23}\text{H}_{22}\text{O}$: C, 87.6; H, 7.06%).

Sensitized Irradiation of the Benzenonaphthalene (1).—Solutions containing the sensitizer used and (1) in Spectrograde dry benzene (4 ml) were prepared as shown in Tables 1 and 2 and Figure 1. These were degassed on a vacuum line (8×10^{-1} Pa) by three freeze-thaw cycles. Irradiation at 3 130 or 2 537 Å was performed with a Ushio 450 W high-pressure mercury lamp

through an appropriate filter system.⁸ [Filter system for 3 130 Å: Pyrex, NiSO₄ (1 kg)/H₂O (1 l), 0.5-cm path length, Toshiba UV-25. Filter system for 2 537 Å: light transmission in 0.5 cm path cell of aqueous solution of 2,7-dimethyl-3,6-diazacyclohepta-2,6-diene perchlorate, 0.4 g/l.] Benzophenone-benzohydrol actinometry was used for the quantum yield determination.⁸ Analyses of products were performed on a Yanako G-180 gas chromatograph (5% OV-17 Chamelite CK 80/60 column 1.5 × 5 mm).

Photoreaction of (1) with Benzaldehyde in the Presence of Cyclohexa-1,3-diene.—Seven benzene solutions each 0.025M in (1), 0.015M in benzaldehyde, and from 0 to 0.11M in cyclohexa-1,3-diene were prepared. Aliquot portions (4 ml) of each solution were placed in the irradiation tubes, degassed, and irradiated for 3 h on the merry-go-round apparatus at 3 130 Å as described in the previous experiment. The amount of the oxete (3) and the cage compound (2) were measured by gas chromatographic analysis as before. The plot of Φ_0/Φ versus [cyclohexa-1,3-diene] for the formation of (2) and (3) gave slopes of 22.8/M = $K_q\tau$.

(4RS,12RS)-1,2,3,4,9,10,11,12-Octahydro-1,4-p-benzenonaphthalene (4) and (4RS,12RS)-1,4,9,10,11,12,13,14-Octahydro-1,4-p-benzenonaphthalene (5).—To a solution of (1) (1 g, 4.8 mmol) and hydrazine hydrate (370 mg, 7.4 mmol) in EtOH-CHCl₃(2:1; 40 ml) was added a 3% solution of H₂O₂ (11 ml) in aqueous ethanol and the mixture was stirred for 24 h at room temperature. After work-up, the solvent was removed under reduced pressure and the residue chromatographed on silica gel eluting with hexane to give (4) and (5) in 40 and 4% yields, respectively: (4), m.p. 116.5–118 °C (EtOH); δ_H (CCl₄) 0.70–1.77 (6 H, m), 2.27 (2 H, m), 2.73 (2 H, m), 3.20 (2 H, m), 6.28 (2 H, sextet, olefinic H distant from benzene ring), and 6.90 (4 H, pseudo s, ArH); ν_{max} (Nujol) 1 628, 1 580, 756, and 730 cm⁻¹; λ_{max} (EtOH) 275 (ϵ 461), 267 (496), 261 (363), and 204 nm (26 500) (Found: C, 91.5; H, 8.65. Calc. for C₁₆H₁₈: C, 91.37; H, 8.63); (5), m.p. 88–89 °C (EtOH); δ_H (CCl₄) 1.00–2.03 (8 H, m), 2.67 (2 H, m), 3.65 (2 H, m), 6.45 (2 H, sextet, olefinic H adjacent to benzene ring), and 6.93 (4 H, pseudo s, ArH); ν_{max} (Nujol) 1 628, 1 580, 756, and 730 cm⁻¹; λ_{max} (EtOH) 273 (ϵ 468), 267 (543), and 207 nm (19 000).

Photoreaction of the Benzenonaphthalene (1) in the Presence of Penta-1,3-diene.—Seven benzene solutions each 0.025M in (1) and from 0 to 0.48M in penta-1,3-diene were prepared. Aliquot portions (4 ml) of each solution were placed in the irradiation

tubes, degassed, and irradiated for 3 h on a merry-go-round apparatus at 3 130 Å as described in the previous experiment. The amount of naphthalene formed was measured by gas chromatographic analysis as before.

Electrolysis of the Benzenonaphthalene (1).—Compound (1) (187 mg, 9×10^{-4} M) was dissolved in acetonitrile (25 ml), and LiClO₄ (100 mg) was added. This stirred mixture, cooled in an ice-water bath, was electrolysed between two stationary platinum plate electrodes at 35–40 V (D.C.) with a current of 100 mA for 5 h. The reaction mixture was then poured into water, extracted with chloroform, and the extract evaporated; the residue when chromatographed on silica gel with hexane as eluant gave naphthalene (96 mg) in 70% yield.

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