

and for the decay in intensity but not for absorption effects.

The direct method program MULTAN²⁰ served to locate the sulfur, oxygen, and the majority of carbon atoms. Several cycles of least-squares refinement followed by the calculation of difference Fourier maps revealed the remaining atoms. Block refinement of the positional and anisotropic thermal parameters of the heavy atoms followed by the positional and isotropic thermal parameters of the hydrogen atoms produced convergence with $R_1 = \sum |F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}$ both equal to 0.051. Anomalous dispersion effects of all non-hydrogen atoms were included in the calculation of F_c using $\Delta F'$ and $\Delta F''$ calculated by Doyle and Turner.²¹ The atomic scattering factors were taken from Cromer and Liberman.²² A list of all interatomic distances and angles are available as supplementary material.

Acknowledgment. We thank the National Science Foundation (CHE 79-03953) and the National Institute of Health (AI-13073) for their generous support of this work. The carbon-13 NMR data reported in this investigation were obtained on the departmental CFT-20 and Varian XL 200 instruments provided by NSF Grants 7842 and CHE 800-4246. We also thank the Purdue University

Biological Magnetic Laboratory (NIH RR01077) for access to the 470-MHz ¹H NMR spectrometer and John Saddler and Phil Hamann for providing those spectra. We also thank Professor W. R. Robinson and A. T. McKenzie of the Purdue University Crystal Structure Facility for their invaluable assistance in interpretation of the X-ray data.

Registry No. 6, 4341-24-6; 7, 35023-83-7; 8, 7214-50-8; 9, 81939-74-4; 10a, 81939-75-5; 10b, 81939-76-6; 11a, 81939-77-7; 11b, 81939-78-8; 12a, 81939-79-9; 12b, 81969-75-7; 13, 81939-80-2; 14, 81939-81-3; 16, 81939-82-4; 19 (isomer 1), 81939-83-5; 19 (isomer 2), 81939-84-6; 20, 81939-85-7; 21, 81939-86-8; 23, 81939-87-9; 25, 81939-88-0; 26, 81939-89-1; 27 (isomer 1), 81939-90-4; 27 (isomer 2), 81939-91-5; 28 (isomer 1), 81939-92-6; 28 (isomer 2), 81939-93-7; 30a (β -sulfoxide isomer), 81940-00-3; 30b (α -sulfoxide isomer), 81940-01-4; 29, 42858-97-9; 31, 81939-94-8; 32, 81939-95-9; 33, 81939-96-0; 34, 81939-97-1; 35, 81969-76-8; 36, 81956-23-2; 37, 81939-98-2; 38, 81939-99-3; ethyl acetoacetate, 141-97-9; ethyl crotonate, 10544-63-5; thiophenol, 108-98-5; trifluoroacetic anhydride, 407-25-0; 1,3-cyclopentanedione, 3008-40-0; 2-bromoethanol, 540-51-2.

Supplementary Material Available: Tables of interatomic distances and angles (6 pages). Ordering information is given on any current masthead page.

Photochemistry of Epoxyquinones. 6.¹ Norrish Type II Photoreaction of 2,3-Dihydro-2,3-epoxy-1,4-naphthoquinone

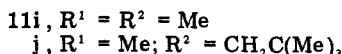
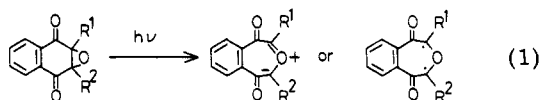
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Photochemical reactions of 2,3-dialkyl-substituted or 2-alkyl-substituted 2,3-dihydro-2,3-epoxy-1,4-naphthoquinones in which the carbonyl group has intramolecularly abstractable γ -hydrogen atoms have been studied. On irradiation, epoxynaphthoquinones 11a-h initially afforded cyclobutanols 12a-h and phthiocols 13a,b. The former are Norrish type II cyclization products, while the latter may be formed via an allene oxide intermediate which is a direct Norrish type II elimination product. The cyclobutanols 12a-h underwent secondary photorearrangement to β -diketones 14a-h and β -alkoxy enones 15a-d,g, but 14g and 14h were readily dehydrated on chromatographic separation over silica gel to give indenone derivatives 15g and 15h. Preference for the Norrish type II photoreaction over the generation of the carbonyl ylide or 1,3-diradical is discussed in terms of the rate constants for each process. A tentative mechanism for the novel photochemical reactions of the cyclobutanols is proposed.

Considerable attention has been focused in recent years on the photochemistry of small-ring heterocyclic compounds.² Among these, investigations of a number of α,β -epoxy ketones 1 have demonstrated that these compounds are photochemically labile, and most can be classified into two groups according to their reaction modes: (a) C_α -O bond cleavage leading to the formation of a 1,3-diradical 2 which would give a β -diketone 3 by 1,2-alkyl migration of either the R^2 or R^3 group and (b) C_α - C_β bond fission leading to the formation of a carbonyl ylide 4a or 1,3-diradical 4b which would give a tetrahydrofuran 5 by 1,3-cycloaddition to olefin (Scheme I). Recently, photochemical generation of the carbonyl ylide 6 or 1,3-diradical 7 from several epoxynaphthoquinones (eq 1) was reported.³



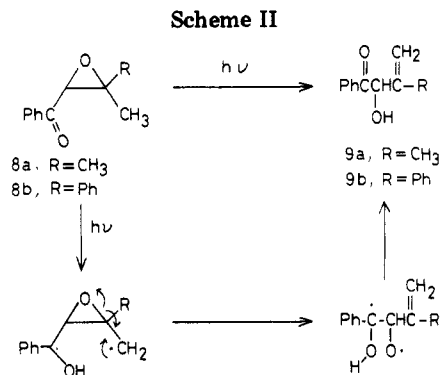
(1) Part 5: Osuka, A., *J. Org. Chem.*, in press.

(2) For reviews, see: (a) Padwa, A. *Org. Photochem.* 1967, 1, 91. (b) Bertoniere, N. R.; Griffin, G. W. *Ibid.* 1973, 3, 138. (c) Griffin, G. W.; Padwa, A. In "Photochemistry of Heterocyclic Compounds"; Buchardt, O., Ed.; Wiley: New York, 1976; p 41. (d) Nastasi, M.; Streith, J. In "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. III, p 381.

These reactive intermediates were successfully trapped by olefins,^{3a} ketones,^{3b} and aldehydes.^{3b} However, irradiation of dimethylacrylophenone oxide (8a) and *trans*-dypnone oxide (8b) were reported to give the unsaturated keto alcohols 9a and 9b, respectively, as the major products⁴. (Scheme II). The absence of detectable amounts of β -diketo products in those cases is noteworthy. The authors

(3) (a) Arakawa, S. *J. Org. Chem.* 1977, 42, 3800. (b) Maruyama, K.; Osuka, A. *Chem. Lett.* 1979, 77.

(4) Zimmerman, H. E.; Cowley, B. R.; Tseng, C.-Y.; Wilson, J. W. *J. Am. Chem. Soc.* 1964, 86, 947.

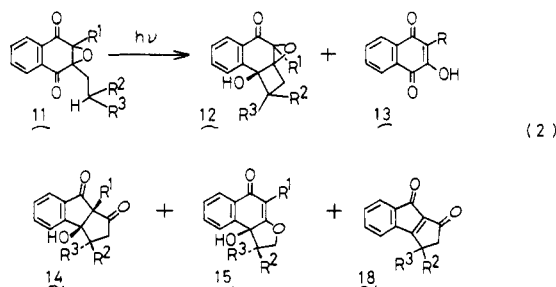


postulated that the reaction proceeds by initial γ -hydrogen abstraction followed by homolytic scission of the oxirane ring. These results suggest the preference of γ -hydrogen abstraction over opening of the oxirane ring (path a or path b in Scheme I) in the reaction of triplet aryl ketones. In this paper, the photochemical reaction of 2,3-dialkyl- or 2-alkyl-substituted 2,3-dihydro-2,3-epoxy-1,4-naphthoquinones in which the carbonyl group has intramolecularly abstractable γ -hydrogen atoms will be described. This paper will reveal that the Norrish type II photoreaction is preferred to the generation of the carbonyl ylide 6 or 1,3-diradical 7.⁵

Results and Discussion

Syntheses of Starting Epoxynaphthoquinones. The synthesis of 2,3-dialkyl-substituted epoxynaphthoquinones 11a-f' was achieved by NaOCl/pyridine epoxidation of 2,3-dialkyl-substituted 1,4-naphthoquinones 10a-f, which, in turn, were prepared by the method of Jacobsen.⁶ 2-Alkyl-substituted epoxynaphthoquinones 11g and 11h were prepared by epoxidation of 2-alkyl-1,4-naphthoquinones 10g and 10h, respectively, with alkaline hydrogen peroxide.⁷

Photoproduct Analysis. Irradiation of a benzene solution of 2-methyl-3-(2-methylpropyl)-2,3-dihydro-2,3-epoxy-1,4-naphthoquinone (11a, 0.02 M) with Pyrex-filtered light with up to 65% conversion of reactant followed by separation over silica gel afforded (eq 2) the cyclobutanol



a, R¹ = R² = R³ = Me; b, R¹ = Me, R², R³ = (CH₂)₃; c-ex, R¹ = R² = Me, R³ = H; c-en, R¹ = R³ = Me, R² = H; d, R¹ = Me, R² = R³ = H; e, R¹ = Me, R² = R³ = Ph; f-ex, R¹ = R³ = Me, R² = Ph; f-en, R¹ = R² = Me, R³ = Ph; g, R¹ = H, R² = R³ = Me; h, R¹ = H, R² = R³ = Ph. 13a, R = Me; 13b, R = H.

12a (25%), the phthiocol 13a (17%), the β -diketone 14a (40%), and the β -alkoxy enone 15a (15%) (Table I). Structure assignments for these photoproducts were made on the basis of characteristic spectral data and elemental

Table I. Type II Photoreaction of Epoxynaphthoquinones

run	reactant	solvent	% conv	product distribution, ^a %			
				12	13	14	15
1	11a	C ₆ H ₆	20	73	8 ^b	12	5
2	11a	C ₆ H ₆	65	25	17 ^b	40	15
3	11a	MeOH	78	63	6 ^b	15	7
4	11b	C ₆ H ₆	42	16	12 ^b	40	10
5	11c	C ₆ H ₆	63	44 ^c	10 ^b	25 ^d	10 ^e
6	11d	C ₆ H ₆ - <i>t</i> -BuOH ^f	87	43	7 ^b	22	g
7	11e	C ₆ H ₆	67	51	15 ^b	g	h
8	11f	C ₆ H ₆ - <i>t</i> -BuOH	59	59.5 ⁱ	15 ^b	23 ^j	h
9	11f'	C ₆ H ₆ - <i>t</i> -BuOH	61	69 ^k	14 ^b	18 ^l	h
10	11g	C ₆ H ₆	48	12	12 ^m	24 ⁿ	14
11	11g	MeOH	63	52	2 ^m	26 ⁿ	10
12	11h	C ₆ H ₆	75	65	5 ^m	28 ⁿ	h

^a Isolated yields based on the amounts of consumed 11. ^b 13a. ^c 12c-ex/12c-en ratio of 1.93. ^d 14c-ex/14c-en ratio of 1.56. ^e 15c-ex/15c-en ratio of 2.33. ^f C₆H₆/Bu-*t*-OH ratio of 1. ^g Not determined. ^h Not detected. ⁱ 12f-ex/12f-en ratio of 0.17. ^j 14f-ex/14f-en ratio of 0.44. ^k 12f-ex/12f-en ratio of 0.13. ^l 14f-ex/14f-en ratio of 0.5. ^m 13b. ⁿ Isolated yields as of the indenone derivatives 18.

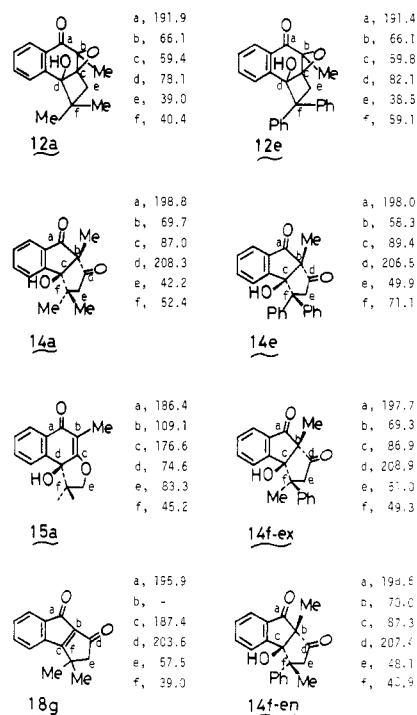


Figure 1. ¹³C NMR (CDCl₃) data (δ) of selected photoproducts.

analyses. The IR spectrum of 12a showed characteristic bands at 3400 (hydroxy) and 1680 (a conjugated ketone) cm⁻¹; the ¹H NMR (CDCl₃) spectrum indicated the presence of three methyl groups at δ 0.84, 1.42, and 1.50 and methylene hydrogens at δ 2.06 and 2.84 (AB q, *J* = 10 Hz). The ¹³C NMR (CDCl₃) of 12a revealed one ketone carbon at δ 191.9, four quaternary carbons at δ 78.1, 66.1, 59.4, and 40.4, and one methylene carbon at δ 39.0, besides three methyl carbons and six aromatic carbons (Figure 1). 2-Hydroxy-3-methyl-1,4-naphthoquinone (13a) was identical with an authentic sample prepared by the treatment of 2-methyl-2,3-dihydro-2,3-epoxy-1,4-naphthoquinone (22) with concentrated sulfuric acid.⁸ The IR spectrum of 14a showed characteristic bands at 3450 (hydroxy), 1750 (a five-membered ketone), and 1715 (a conjugated five-

(5) For preliminary reports on some aspects on the present study, see: (a) Maruyama, K.; Osuka, A.; Suzuki, H. *J. Chem. Soc., Chem. Commun.* 1980, 323. (b) Jimentz, M.; Rodriguez-Hahn, L.; Romo, J. *Latinoam. Quim.* 1974, 5, 184.

(6) Jacobsen, N.; Torsell, K. *Justus Liebigs Ann. Chem.* 1972, 763, 135.

(7) Marmor, S. *J. Org. Chem.* 1963, 28, 250.

(8) Fieser, L. F. *J. Biol. Chem.* 1940, 133, 391.

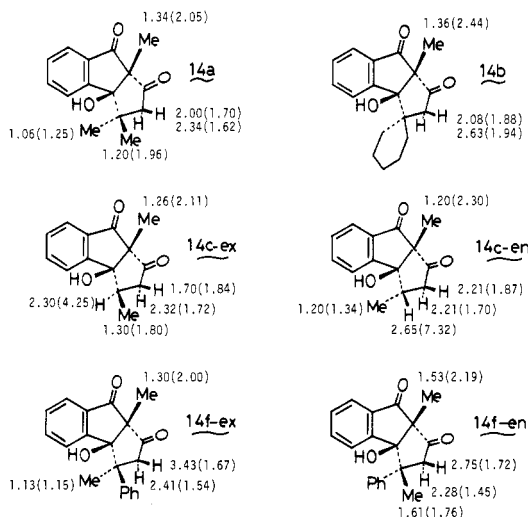
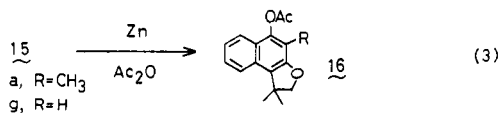


Figure 2. ¹H NMR assignments for 14 with Eu(dpm)₃ induced shifts given in parentheses. The induced shifts were determined from the plots of shifts (in ppm) vs. the molar ratio of Eu(dpm)₃/14 by the least-squares method; concentrations of 14 were ca. 0.125 M in CDCl₃.

membered ketone) cm⁻¹; the ¹H NMR (CDCl₃) spectrum indicated the presence of three methyl groups at δ 1.06, 1.20, and 1.34 and methylene hydrogens at δ 2.04 and 2.28 (AB q, *J* = 15 Hz). The ¹³C NMR (CDCl₃) spectrum of 14a revealed the presence of two ketone carbons at δ 208.3 and 198.8, three quaternary carbons at δ 87.0, 69.7, and 52.4, and one methylene carbon at δ 42.2, besides three methyl carbons and six aromatic carbons. The stereochemistry of the ring junction of the β-diketone 14a was assigned to be cis-fused on the basis of changes in the chemical shifts of its protons on addition of the shift reagent, tris(dipivalomethanato)europium(III) [Eu(dpm)₃, Figure 2].⁹ This assignment was confirmed by the fact that 14a did not isomerize at all on treatment with hydrochloric acid in chloroform even at elevated temperature, since the trans isomer would readily isomerize on acid treatment due to its highly strained structure. The IR spectrum of 15a showed characteristic bands at 3320 (hydroxy) and at 1650 and 1635 (a conjugated ketone) cm⁻¹; the ¹H NMR (CDCl₃) spectrum indicated the presence of three methyl groups at δ 0.82, 1.54, and 1.66 and methylene hydrogens adjacent to the oxygen at δ 3.96 and 4.56 (AB q, *J* = 7 Hz). The data from the ¹³C NMR (CDCl₃) spectrum of 15a were consistent with the assigned structure: δ 186.4 (s, a conjugated ketone), 176.6 (s, β-carbon of β-alkoxy enone), 109.1 (s, α-carbon of β-alkoxy enone), 83.2 (t), 76.4 (s), 45.2 (s), besides three methyl carbons and six aromatic carbons. The UV (EtOH) spectral properties of 15a also indicated α,β-unsaturated aryl ketone: λ_{max} 315 nm (ε 5000), 292 (6150). Further, reductive acetylation (Zn/Ac₂O) of 15a yielded naphthalene derivative 16a in a yield of 75% (eq 3).



(9) Although in the preliminary paper^{5a} we erroneously assigned a trans-fused structure for the β-diketone, it should be corrected to the cis-fused. In ref 5a, the assignment was only based on the comparison of the chemical shift of methyl protons of 14e (at δ 1.36) with that of its acetate (at δ 1.36). However, acetylation of 14e was carried out under acidic conditions (HClO₄/Ac₂O), where *trans*-14e should isomerize to thermodynamically stable *cis*-14e. Further, the comparison of the chemical shifts of methyl protons of 14 with those of their acetates in the series appeared to provide support for the *cis*-fused structure (Figure 4).

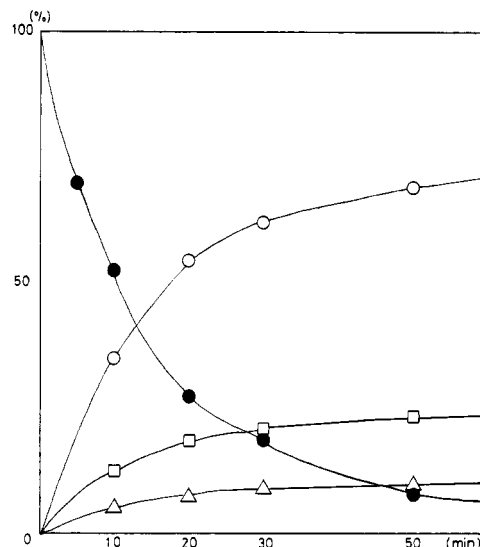


Figure 3. Photochemical reaction of the cyclobutanol 12a in benzene. The solid circles show the amount of 12a, while open symbols (O, □, and Δ) represent the amount of 14a, 15a, and 13a, respectively.

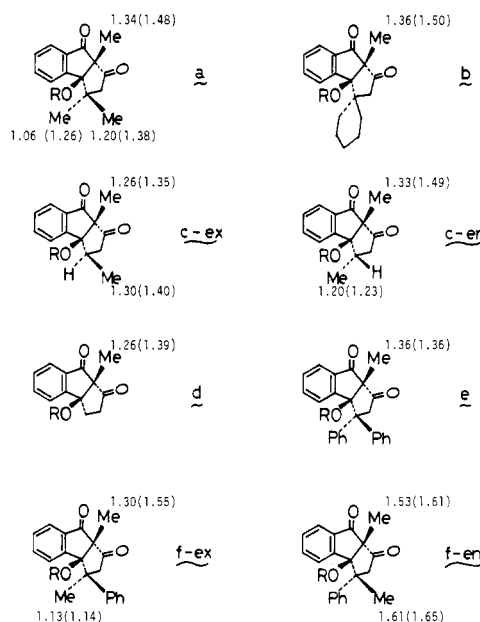
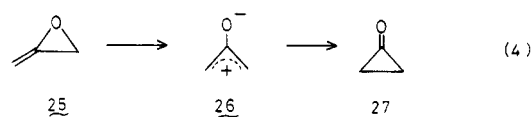


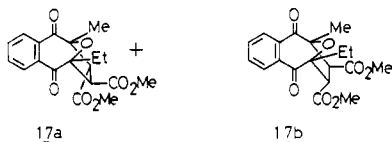
Figure 4. Comparison of the chemical shifts of methyl groups of 14 (R = H) with those of 35 (R = Ac), given in parentheses.



Controlled experiments revealed that the cyclobutanol 12a and the phthiocol 13a were the primary photoproducts (12a/13a ratio of 10) arising from a type II reaction, and upon continued irradiation 12a was transformed into 13a, 14a, and 15a. High-pressure liquid chromatography (HPLC) analysis of the irradiation of 12a (0.015 M) in benzene revealed that the ratio of 13a/14a/15a was constant (1:6.5:2.5) during the irradiation, indicating that no interconversion of either 13a, 14a, or 15a was operative under the reaction conditions (Figure 3). The cyclobutanol 12a was obtained in a higher yield (63%) by irradiating 11a for a suitable time in methanol, where the efficiency of the type II reaction was greatly enhanced by biradical solvation but where that of the secondary photoreaction of 12a was not so influenced.

Further examples which would support the generality of the preference of the intramolecular γ -hydrogen abstraction over the generation of the carbonyl ylide or 1,3-diradical and succeeding photochemical rearrangement of the cyclobutanol 12 were sought. With this in mind, the photochemical behavior of a number of epoxy-naphthoquinones which contain γ -hydrogen atoms was investigated. In each case, cyclobutanol 12 and phthiocol 13, arising from intramolecular γ -hydrogen atom abstraction, and rearranged products, arising from cyclobutanol 12, were observed. Irradiation of 2-methyl-3-(cyclohexylmethyl)-2,3-dihydro-2,3-epoxy-1,4-naphthoquinone (11b) in benzene gave the cyclobutanol 12b (16%), 13a (12%), the β -diketone 14b (40%), and the β -alkoxy enone 15b (10%). The latter two products were secondary photoproducts derived from 12b. Similar irradiation of 2-methyl-3-propyl-2,3-dihydro-2,3-epoxy-1,4-naphthoquinone (11c) in benzene gave the epimeric cyclobutanols 12c-ex (29%) and 12c-en (15%), 13a (10%), the epimeric β -diketones 14c-ex (14%) and 14c-en (9%), and the epimeric β -alkoxy enones 15c-ex (7%) and 15c-en (3%). The stereochemistry at C-10 position of 12c was assigned on the basis of the chemical shifts of methyl protons at C-10. The methyl protons of 12c-en appeared at higher field (δ 0.80) due to the shielding effects of benzene ring, compared with those of 12c-ex appearing at δ 1.42. A separate irradiation of the cyclobutanol 12c-ex in benzene gave only 14c-ex, 15c-ex, and 13a, and, similarly, 12c-en gave only 14c-en, 15c-en, and 13a, indicating that the photorearrangement of 12c to 14c and 15c proceeds without epimerization of methyl group at C-10.

Irradiation of 2-ethyl-3-methyl-2,3-dihydro-2,3-epoxy-1,4-naphthoquinone (11d) in benzene led only to poorer yields of type II photoproducts, accompanied by the formation of many unidentified products. On the other hand, the cyclobutanol 12d and the phthiocol 13a were obtained in 43% and 7% yields, respectively, by irradiating 11d in benzene-*t*-BuOH (1:1). Again, the cyclobutanol 12d was found to undergo photochemical rearrangement to the β -diketone 14d (52%) and the β -alkoxy enone 15d (22%) and photoelimination to 13a (9%). In the photochemistry of 11d, competitive generation of the carbonyl ylide or 1,3-diradical appeared to be responsible for the lower yields of type II photoproducts. In fact, irradiation of a benzene-*t*-BuOH (1:1) solution of 11d (0.05 M) and dimethyl fumarate (0.07 M) resulted in the formation of a 1:1 mixture of isomeric adducts 17a and 17b (31%), arising



from 1,3-cycloaddition of a carbonyl ylide or a 1,3-diradical to dimethyl fumarate, along with type II photoproducts 12d (24%) and 13a (4%).

When irradiation of 2-methyl-3-(2,2-diphenylethyl)-2,3-dihydro-2,3-epoxy-1,4-naphthoquinone (11e) was carried out in benzene up to 67% conversion, the cyclobutanol 12e (51%), 13a (15%), 1,1-diphenylethylene (8%), and the β -diketone 14e (22%) were obtained. The photochemistry of 12e stands in contrast to those of 12a-d in view of the facts that 12e gave a significant amount of 11e along with 13a and 14e and that no sign of the formation of 15e could be detected. This can be interpreted as direct evidence for competitive C₁-C₁₀ bond rupture leading to the formation of a type II biradical, which will produce 11e by reverse hydrogen transfer (disproportionation).

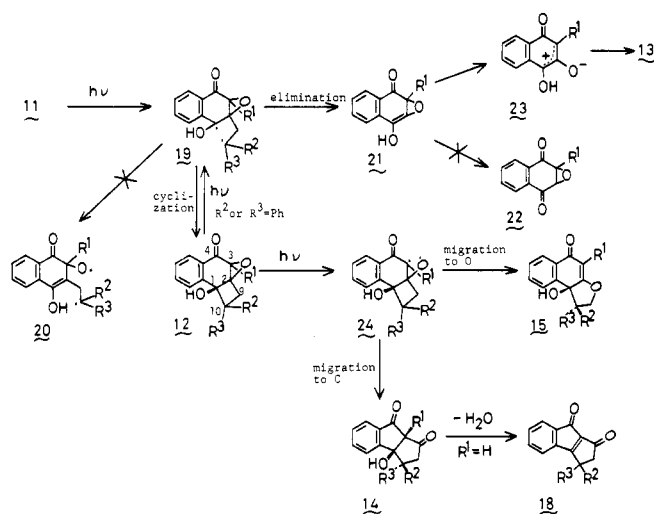
Epoxidation of 2-methyl-3-(2-phenylpropyl)-1,4-naphthoquinone (10f) gave a 1:1 mixture of diastereoisomeric epoxy-naphthoquinones which could be separated by repeated column chromatography over silica gel, giving 11f (mp 76-78 C) and 11f' (mp 83.5-84.5 C). Irradiation of either 11f or 11f' resulted in the almost same product distribution: 11f gave the epimeric cyclobutanols 12f-ex (51%) and 12f-en (8.5%), 13a (15%), and the epimeric β -diketones 14f-ex (16%) and 14f-en (7%), while 11f' gave 12f-ex (61%), 12f-en (8%), 13a (14%), 14f-ex (12%), and 14f-en (6%). In each case, the corresponding β -alkoxy enone 15f was not detected in the crude photolysate, but 2-phenylpropene was detected by GC analysis in about 10%. The stereochemistry of 12f-ex and 12f-en was assigned on the basis of the chemical shifts of methyl protons at C-10. The methyl protons of 12f-ex appeared at δ 1.23, while those of 12f-en appeared at δ 1.56. In contrast to the photochemical behavior of 12c-ex and 12c-en, a separate irradiation of 12f-ex in benzene gave rise to a 2:1 epimeric mixture of 14f-ex and 14f-en, along with small amount of 11f, 11f', and 13a, suggesting competitive C₁-C₁₀ bond rupture in 12f.

The photochemical reactions of 2-alkyl-substituted epoxy-naphthoquinones 11g and 11h have also been studied. Irradiation of 2-(2-methylpropyl)-2,3-dihydro-2,3-epoxy-1,4-naphthoquinone (11g) in methanol with up to 63% conversion followed by the separation over silica gel afforded the cyclobutanol 12g (52%), 2-hydroxy-1,4-naphthoquinone 13b (2%), the β -alkoxy enone 15g (10%), and the indenone derivative 18g (26%). The last product seemed to arise from the dehydration of the expected β -diketone 14g. In fact, ¹H NMR examination of the crude photolysate of 12g in benzene showed no peaks due to 18g but instead a set of two methyl singlets at δ 0.76 and 1.33, an AB quartet at δ 2.15 and 2.68 (J = 15 Hz), and a singlet at δ 3.44, presumably due to 14g. On treatment of this crude photolysate with silica gel in benzene at room temperature, one observed rapid appearance of ¹H NMR signals due to 18g as well as rapid disappearance of the signals mentioned above. Consequently, the indenone derivative 18g is not a direct photolysis product from 12g but is formed from a precursor, maybe 14g, which is readily dehydrated on treatment with silica gel. Similar irradiation of 2-(2,2-diphenylethyl)-2,3-dihydro-2,3-epoxy-1,4-naphthoquinone (11h) in benzene gave the cyclobutanol 12h (65%), 13b (5%), 1,1-diphenylethylene (4%), and the β -alkoxy enone 14h (30%, determined by ¹H NMR). The last product, which was only detected by ¹H NMR spectroscopy [at δ 2.68 and 3.00 (AB q, J = 15 Hz) and 3.40 (s, 1 H)], was isolated as the indenone derivative 18h (28%) after chromatographic separation over silica gel. No sign of the formation of 15h could be detected in this case as well as 11e, 11f, and 11f'.

Reaction Mechanism. The formation of the cyclobutanols 12 and 2-hydroxy-1,4-naphthoquinones 13 can be readily accounted for in terms of a type II process. A biradical 19 is initially formed by γ -hydrogen atom abstraction. Cyclization of the biradical yields the cyclobutanol 12, while direct elimination probably results in the formation of the phthiocol 13. The preferential cyclization of 19 is consistent with previous reports for rigid systems, where elimination would produce highly strained bicyclic compounds with bridgehead double bonds, e.g., α -adamantylacetone^{10a} and α -adamantylacetophenone.^{10b} Mechanistic details of the photoelimination to give 13 are not

(10) (a) Gagosian, R. B.; Dalton, J. C.; Turro, N. J. *J. Am. Chem. Soc.* 1970, 92, 4752. (b) Lewis, F. D.; Johnson, R. W.; Kory, D. R. *Ibid.* 1974, 96, 6100.

Scheme III



yet understood, but the formation of 13 should be correlated with intramolecular γ -hydrogen abstraction because none of 13a was detected in the photolysis of 2,3-dimethyl-2,3-dihydro-2,3-epoxy-1,4-naphthoquinone (11i) or 2-methyl-3-(2,2-dimethylpropyl)-2,3-dihydro-2,3-epoxy-1,4-naphthoquinone (11j). Further, it may be said that elimination occurs prior to a possible epoxy carbonyl rearrangement, judged by the absence of products derived from a radical 20. It is proposed that direct elimination of 19 yields an allene oxide 21 as a transient intermediate (Scheme III), which undergoes isomerization to 13. The absence of 22 in the reaction mixture appears to imply that the keto-enol tautomerization is of minor importance in 21. This observation is consistent with the suggestion that allene oxide undergoes facile isomerization to cyclopropanone via an oxyallyl intermediate.¹¹ In the expected oxyallyl zwitterion 23 arising from isomerization of 21, intramolecular proton transfer could produce 13. There have been earlier reports in which type II photoelimination results in the formation of highly strained species involving an oxygen-containing three-membered ring. Phenylloxirene 29 has been proposed as an intermediate in type II pho-



toelimination of β,γ -epoxy ketone 28,¹² although the intervention of oxirene in this process seems to be rather controversial.¹³

Quantum yields for the disappearance of epoxy-naphthoquinones 11a-h in benzene and benzene-*t*-BuOH (1:1) were determined by using valerophenone as the chemical actinometer.¹⁴ The results are shown in Table II. The increase in quantum yield with added alcohol can be attributed to biradical solvation, which suppresses reversion of the biradical to ground-state epoxy-naphthoquinone.¹⁶ Rate constants for γ -hydrogen abstraction were determined by standard Stern-Volmer quenching experiments in degassed benzene solution with naphthalene as

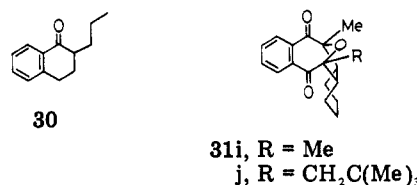
the triplet quencher. From the slopes of the linear Stern-Volmer plots ($k_q\tau$) and the assumption that $k_q = 5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ in benzene solution,¹⁵ values of the triplet lifetime (τ) are obtained. In view of the short triplet lifetime ($\tau < 10^{-8} \text{ s}$), it is unlikely that radiationless decay competes with γ -hydrogen abstraction. Thus, the triplet lifetime is determined by the rate of γ -hydrogen abstrac-

Table II. Quantum Yields and Kinetic Data for the Type II Photoreaction of Epoxynaphthoquinones

epoxynaphthoquinone ^a	ϕ^b		$k_q\tau^c$ M^{-1}	$10^{-8}1/\tau$, s^{-1}
	C_6H_6	C_6H_6 - <i>Bu-t</i> -OH		
11a	0.082	0.49	13	3.7
11b	0.085		5.4	9.1
11c	0.11		23	2.2
11d	0.27		58	0.86
11e	0.18	0.32	3.8	13
11f	0.23	0.60	7.5	6.7
11f'	0.25		7.2	7.1
11g	0.067		10	5.0
11h	0.36	0.54	2.8	18
30 ^d	0.12	0.39 ^e	8.5 ^f	5.9

^a Concentration of epoxynaphthoquinone of ca. 0.015 M. ^b Quantum yields for the disappearance of epoxy-naphthoquinones $\pm 10\%$. ^c Least-squares slope of linear Stern-Volmer plots in benzene solution with naphthalene quencher ($\pm 10\%$). ^d From ref 10b. ^e Quantum yield in *i*-PrOH. ^f Using *trans*-1,3-pentadiene as the triplet quencher.

tion ($1/\tau = \kappa_\gamma$). Lewis' results^{10b} for 2-propyl-1-tetralone (30) in benzene and *i*-PrOH are included in Table II for



purposes of comparison. The reactivity of the $n\pi^*$ triplet of 11 toward γ -hydrogen abstraction is determined primarily by the γ C-H bond strength. Inductive effects¹⁶ by electron-withdrawing substituents such as the *o*-acyl group and the α -oxyranyl group and less conformational mobility^{10b} imposed by the oxirane ring might enhance the triplet reactivity of 11, but the value of k_γ for 11c was only 37% as much as that of 30. These results might be simply accounted for in view of lower triplet energy of 11c, compared with that of 30. Type II photoreaction of 11 was quenched by naphthalene ($E_T = 61 \text{ kcal/mol}$) but only inefficiently by biphenyl ($E_T = 66 \text{ kcal/mol}$), indicating the triplet energies of 11 to be significantly lower than those of alkyl phenyl ketones ($E_T = 72\text{--}73 \text{ kcal/mol}$).

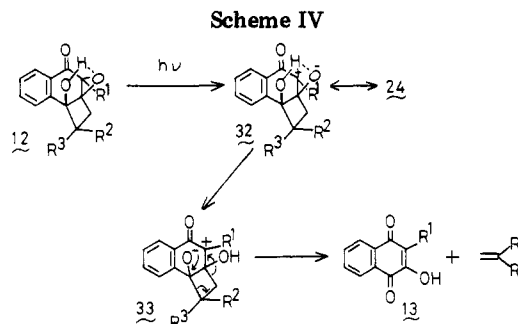
In contrast to type II photoreaction of 11a-h, excitation of 11i or 11j gives rise exclusively to the generation of the carbonyl ylide or 1,3-diradical, which can be trapped by suitable dipolarophiles.³ It is of mechanistic interest to compare the rate of the opening of the oxirane ring (k_o) with that of the γ -hydrogen abstraction (k_γ). In the case of 11d, the opening of the oxirane ring occurs competitively with type II process. Both processes were quenched by naphthalene with equal efficiency, indicating that they

(11) Chan, J. H.; Ong, B. S. *J. Org. Chem.* 1978, 43, 2994.(12) Padwa, A.; Crumrine, D.; Hartman, R.; Layton, R. *J. Am. Chem. Soc.* 1967, 89, 4435.(13) Cormier, R. A. *Tetrahedron Lett.* 1980, 2021.(14) Wagner, P. J.; Kochevar, I. E. *J. Am. Chem. Soc.* 1972, 94, 7489.(15) Wagner, P. J.; Kochevar, I. E. *J. Am. Chem. Soc.* 1968, 90, 2232.(16) Wagner, P. J. *Acc. Chem. Res.* 1971, 4, 168.

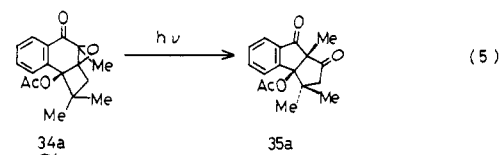
occurred from the same excited state, presumably the $n\pi^*$ triplet state. Since both the cyclobutanol **12d** and the 1,3-dipolar cycloadducts **17a** and **17b** are photolabile under the reaction conditions, the chemical yields of **12d** and **17a,b** do not accurately reflect the relative propensities for the type II process and the opening of the oxirane ring. However, the relative product yields suggest the nearly same rate constants of two processes in triplet **11d**. Degassed benzene solutions, 0.015 M in **11i** or **11j** and 0.02 M in cyclohexene containing various concentrations of naphthalene, were irradiated in parallel with valero-phenone actinometer.¹⁷ Quantum yields for the formation of the cycloadducts **31i** and **31j** were 0.35 for **11i** and 0.70 for **11j**, respectively. Stern-Volmer plots were linear to $\Phi^0/\Phi = 6$ for both epoxynaphthoquinones, with slopes ($k_q\tau$) of 99 M^{-1} for **11i** and 20 M^{-1} for **11j**. With $k_q = 5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, $1/\tau = 5.1 \times 10^7 \text{ s}^{-1}$ for triplet **11i** and $2.5 \times 10^8 \text{ s}^{-1}$ for triplet **11j**. If it is assumed that the triplet lifetimes of **11i** and **11j** are largely determined by the rate of the opening of the oxirane ring (k_o), the values of $1/\tau$ can be regarded as k_o . The k_o for **11j** is a factor of 5 higher than that for **11i**. It thus appears that there are steric acceleration effects in the opening of the inner C-C bond of the oxirane ring in epoxynaphthoquinones. Although how these effects might enhance k_o in **11a-h** is not known, it can be said that values of k_o are much smaller than those of k , on the basis of the amounts of type II photoproducts which account for nearly all of the products.

The photorearrangement of the cyclobutanol **12** to the β -diketone **14** and the β -alkoxy enone **15** can be best explained in terms of an initial $\text{C}_\alpha\text{-O}$ bond cleavage to give a diradical **24**, followed by migration of the benzyl group to the α -carbon (*migration to C*) or migration of methylene group to the oxygen (*migration to O*). To the best of our knowledge, 1,2-alkyl migration to the oxygen atom is unprecedented in spite of its formal possibility, although the photochemistry of α,β -epoxy ketones has been studied extensively.² A possible explanation for the unprecedented migration to O may be that the reaction proceeds in such a concerted manner that the methylene group has to be attached to the backside lobe of the bond to be cleaved. Thus, migration to C of the methylene group would be greatly disfavored by reason of steric factors. If such a concerted migration occurs, migration to C of the benzyl group would lead to the *trans* isomer of **14**. Unfortunately, because the *cis* stereochemistry of **14** may be the result of control by thermodynamic factors (the *trans* isomer of **14** would be highly strained), no definitive conclusions relating to the timing of the **12** to **14** and **15** rearrangement can be drawn at this time.

As for the mechanism of photoelimination to **13** from **12**, one may envision a route involving $\text{C}_1\text{-C}_{10}$ bond rupture, resulting in the formation of type II biradical **19**, which could produce **13** by elimination. This is the case for the cyclobutanols **12e**, **12f-ex** and **12f-en**, which, on excitation, give epoxynaphthoquinones by disproportionation of **19** as well as produce **13a**. However, none of the epoxynaphthoquinones **11a-d** could be detected in the irradiation of **12a-d** in benzene even at the early stages of the reaction. Further, in the case of **12c-ex** or **12c-en** once $\text{C}_1\text{-C}_{10}$ bond fission occurred, there should be brought



about concomitant epimerization of the methyl group in **12c**, **14c**, and **15c**. Therefore, there seems to exist, besides $\text{C}_1\text{-C}_{10}$ bond fission, an alternative route to **13a** from **12a-d**. Scheme IV shows a possible route to **13a** from **12a-d**, which begins with heterocyclic $\text{C}_3\text{-O}$ bond cleavage followed by proton transfer to give an intermediate, **33**, which finally gives **13a**. It is not unreasonable that the hydroxy group at the C-1 position of **12** will interact through hydrogen bonding with the oxirane oxygen, which will become slightly electron rich on excitation. Thus, the cyclobutanol **12a** was esterified ($\text{HClO}_4/\text{Ac}_2\text{O}$, -20°C), and the photochemistry of the acetate **34a** was examined. Irradiation of **34a** in benzene afforded only β -diketone acetate **35a** (eq 5) in 52% but neither migration to O



product nor elimination product was not observed. This result seems to suggest an unique role of the hydroxy group at C-1 in the photochemistry of cyclobutanol. The strain arising from spiro-fused structure of **12** also appears to play an important role in its photochemistry; however, speculation regarding the detailed reaction mechanism is unwarranted at present.

In summary, the type II photoprocess is preferred to generation of the carbonyl ylide or 1,3-diradical in the photochemistry of epoxynaphthoquinones which contain γ -hydrogen atoms. Type II cyclization gives highly strained cyclobutanol in a good yield, which is transformed into a novel class of polycondensed ring compounds, while type II elimination presumably gives allene oxide which undergoes facile isomerization to phthiocol.

Experimental Section

Melting points were measured on a Yanagimoto micro melting point apparatus and are uncorrected. Infrared spectra were recorded on a Hitachi Model 260-10. ^1H NMR spectra were recorded on a JEOL PS-100, and chemical shifts are reported in parts per million on the δ scale from internal Me_4Si . ^{13}C NMR spectra were recorded on a JEOL FX-100. Elemental analyses were performed at the Microanalytical Laboratory of Kyoto University. High-pressure liquid chromatography (HPLC) analyses were performed on a JASCO Model FLC A-700 equipped with a UV detector (Model UVIDEC-100). The separations were made on a $500 \times 2 \text{ mm}$ stainless-steel column packed with JASCO-Pack SS-05 with a water-saturated mixture of hexane and ether as the eluent. GC analyses were performed on a Hitachi Model 163, using a $3 \text{ mm i.d.} \times 1 \text{ m}$ stainless-steel column packed with 10% SE-30 on Celite 545 AW. Preparative separations were performed by column chromatography over silica gel (Wakogel C-200). UV irradiations were carried out in a Pyrex vessel (Ei-

(17) The total amounts of 1,3-dipolar cycloadducts **34i** and **34j** and their secondary photoproducts accounted for nearly all of the products produced in the reaction of **11i** and **11j** with cyclohexene. Triplet states of **11i** and **11j** were slightly quenched by electron-rich olefins but 0.02 M cyclohexene affected the triplet lifetimes of **11i** and **11j** at most less than 2%. Osuka, A.; Suzuki, H.; Maruyama, K., *J. Chem. Soc., Perkin Trans. 1*, in press.

Table III. Properties of 1,4-Naphthoquinones 10

compd ^a	yield, %	mp, °C	IR (KBr), cm ⁻¹	¹ H NMR (CDCl ₃), δ
10a	66	oil	2940, 1660, 1600, 1290, 710	0.96 (d, <i>J</i> = 6 Hz, 6 H), 1.90 (m, 1 H), 2.06 (s, 3 H), 2.54 (d, <i>J</i> = 6 Hz, 2 H), 7.5-7.6 (m, 2 H), 7.9-8.0 (m, 2 H)
10b	41	68-69.5	2910, 1660, 1650, 1600, 1300, 710	0.9-1.9 (m, 11 H), 2.2 (s, 3 H), 2.58 (d, <i>J</i> = 6 Hz, 2 H), 7.6-7.8 (m, 2 H), 8.0-8.2 (m, 2 H)
10c	62	60-61	2960, 1670, 1630, 1600, 1300, 730	1.02 (t, <i>J</i> = 6 Hz, 3 H), 1.54 (m, 2 H), 2.08 (s, 3 H), 2.60 (t, <i>J</i> = 6 Hz, 2 H), 7.6-7.7 (m, 2 H), 7.9-8.1 (m, 2 H)
10d	43	67-68	2960, 1660, 1620, 1600, 1300, 710	1.10 (t, <i>J</i> = 6 Hz, 3 H), 2.15 (s, 3 H), 2.63 (q, <i>J</i> = 6 Hz, 2 H), 7.6-7.7 (m, 2 H), 7.9-8.1 (m, 2 H)
10e	62	114-115	1660, 1600, 1300, 700	1.74 (s, 3 H), 3.38 (d, <i>J</i> = 7 Hz, 2 H), 4.27 (t, <i>J</i> = 7 Hz, 1 H), 7.2-7.3 (m, 10 H), 7.6-7.7 (m, 2 H), 8.0-8.1 (m, 2 H)
10f	52	72-74	2960, 1660, 1600, 1310, 710	1.35 (d, <i>J</i> = 6 Hz, 3 H), 1.90 (s, 3 H), 2.7-3.1 (m, 3 H), 7.1-7.2 (m, 5 H), 7.6-8.1 (m, 4 H)
10g	61	oil	2960, 1670, 1600, 1300, 1270, 780	0.98 (d, <i>J</i> = 6 Hz, 6 H), 1.95 (m, 1 H), 2.50 (d, <i>J</i> = 6 Hz, 2 H), 6.75 (s, 1 H), 7.6-8.2 (m, 4 H)
10h	53	97.5-98	1660, 1600, 1300, 720	3.22 (d, <i>J</i> = 8 Hz, 2 H), 4.30 (t, <i>J</i> = 8 Hz, 1 H), 6.35 (s, 1 H), 7.0-7.2 (m, 10 H), 7.4-8.0 (m, 4 H)

^a Satisfactory C and H elemental analyses were obtained for all compounds in this table.

Table IV. Properties of Epoxynaphthoquinones 11

compd ^a	yield, %	mp, °C	IR (KBr), cm ⁻¹	¹ H NMR (CDCl ₃), δ
11a	87	56-57	2960, 1695, 1600 1310, 710	0.98 (d, <i>J</i> = 4 Hz, 3 H), 1.01 (d, <i>J</i> = 4 Hz, 3 H), 1.72 (s, 3 H), 1.9-2.2 (m, 3 H), 7.6-7.8 (m, 2 H), 7.9-8.0 (m, 2 H)
11b	92	78-79	2940, 1700, 1600, 1330, 1310, 710	0.9-2.2 (m, 13 H), 1.7 (s, 3 H), 7.6-8.1 (m, 4 H)
11c	84	oil	2950, 1700, 1590 1310, 710	0.98 (t, <i>J</i> = 6 Hz, 3 H), 1.63 (s, 3 H), 1.3-1.9 (m, 2 H), 2.0-2.3 (m, 2 H), 7.6-7.8 (m, 2 H), 7.9-8.0 (m, 2 H)
11d	87	37-37.5	3020, 2960, 1700, 1600, 1300, 710	1.10 (t, <i>J</i> = 7 Hz, 3 H), 1.7 (s, 3 H), 1.6-2.5 (m, 2 H), 7.6-7.8 (m, 2 H), 7.9-8.0 (m, 2 H)
11e	92	128-128.5	1695, 1600, 1310, 710	1.18 (s, 3 H), 2.62 (dd, <i>J</i> = 10, 14 Hz, 1 H), 3.05 (dd, <i>J</i> = 14 Hz, 1 H), 4.50 (dd, <i>J</i> = 5, 10 Hz, 1 H), 7.0-7.3 (m, 10 H), 7.6-7.8 (m, 2 H), 7.8-8.0 (m, 2 H)
11f	41	76-78	2950, 1700, 1600 1300, 720	1.08 (s, 3 H), 1.40 (d, <i>J</i> = 7 Hz, 3 H), 1.98 (dd, <i>J</i> = 10, 14 Hz, 1 H), 2.66 (dd, <i>J</i> = 6, 14 Hz, 1 H), 3.32 (dd, <i>J</i> = 6, 10 Hz, 1 H), 7.1-7.3 (m, 5 H), 7.6-7.8 (m, 2 H), 7.9-8.0 (m, 2 H)
11f'	39	83.5-84.5	2950, 1695, 1600, 1300, 710	1.31 (d, <i>J</i> = 7 Hz, 3 H), 1.74 (s, 3 H), 2.4-2.5 (m, 2 H), 3.16 (m, 1 H), 7.1-7.3 (m, 5 H), 7.6-7.8 (m, 2 H), 7.9-8.0 (m, 2 H)
11g	62	oil	2950, 1700, 1590, 1300, 720	0.94 (d, <i>J</i> = 6 Hz, 3 H), 0.98 (d, <i>J</i> = 6 Hz, 3 H), 1.53 (dd, <i>J</i> = 6, 15 Hz, 1 H), 1.95 (m, 1 H), 2.33 (dd, <i>J</i> = 5, 15 Hz, 1 H), 3.81 (s, 1 H), 7.5-8.0 (m, 4 H)
11h	73	116-117	1700, 1600, 1500, 1300, 710	2.12 (dd, <i>J</i> = 10, 12 Hz, 1 H), 3.14 (s, 1 H), 3.37 (dd, <i>J</i> = 6, 12 Hz, 1 H), 4.35 (dd, <i>J</i> = 6, 10 Hz, 1 H), 7.0-7.3 (m, 10 H), 7.6-8.0 (m, 4 H)

^a Satisfactory C and H elemental analyses were obtained for all compounds in this table.

kosha EHB-WF) under an argon atmosphere with an Eikosha 300-W high-pressure Hg lamp.

Preparation of Epoxynaphthoquinones. The epoxy-naphthoquinones used were prepared by epoxidation of the corresponding naphthoquinone with NaOCl/pyridine or alkaline H₂O₂.^{1,3a} The naphthoquinones were synthesized by the method of Jacobsen.⁶ Isolated yields and physical properties are summarized in Tables III and IV.

General Procedure for the Photochemical Reactions of 11. A solution of 11 (1 g) in 400 mL of benzene in a Pyrex vessel was bubbled with argon for 10 min and then irradiated under cooling with water for a suitable time. The progress of the reaction was followed by HPLC. After removal of the solvent, the residual oil was separated by chromatography on a silica gel column with ether/hexane as the eluant. Final purification was usually accomplished by preparative TLC and recrystallization. Physical properties of photoproducts are summarized in Tables V-VII.

Reductive Acetylation of the β-Alkoxy Enone 15a. A solution of 15a (70 mg), anhydrous NaOAc (130 mg), and Zn dust (700 mg) in 5 mL of acetic anhydride was refluxed for 30 min. The

reaction mixture was poured into 50 mL of saturated NaHCO₃ solution and extracted with two portions of CH₂Cl₂ (50 mL), and the organic extracts were washed with water before being dried (Na₂SO₄). Removal of the solvent afforded crude product, which was purified on a short column of silica gel, giving 16a (58 mg, 75%).

8-Acetoxy-3,3,9-trimethyl-2,3-dihydronaphthaleno[1,2-*b*]furan (16a): mp 96-98 °C; IR (KBr) 2940, 1750 (ester C=O), 1360, 1200, 1190, 1075, 760 cm⁻¹; ¹H NMR (CDCl₃) δ 1.58 (s, 6 H), 2.18 (s, 3 H), 2.44 (s, 3 H), 4.34 (s, 3 H), 7.2-8.0 (m, 4 H); ¹³C NMR (CDCl₃) δ 10.0 (q), 20.5 (q), 27.2 (q), 43.8 (s), 85.5 (t), 114.8 (s), 121.9 (d), 122.2 (d), 122.9 (d), 123.3 (s), 125.3 (s), 125.9 (d), 128.7 (s), 144.8 (s), 156.2 (s), 168.4 (s). Anal. Calcd for C₁₇H₁₈O₃: C, 75.53; H, 6.71. Found: C, 75.50; H, 6.68.

Irradiation of the Cyclobutanols 12c-ex and 12c-en in Benzene. A solution of 12c-ex (100 mg) in 25 mL of benzene was irradiated for 1 h. Separation of the products by column chromatography gave 13a (8 mg, 10%), 14c-ex (35 mg, 35%), and 15c-ex (17 mg, 17%). A solution of 12c-en (100 mg) in 25 mL of benzene was irradiated for 1 h. Separation of the products by

Table V. Properties of Cyclobutanols 12

compd ^b	mp, °C	IR (KBr), cm ⁻¹	¹ H NMR (CDCl ₃), δ
12a	143-144	<i>a</i>	7.1-7.5 (m, 3 H), 7.9 (m, 1 H) ^a
12b	159-161	3500, 2940, 1675, 1600, 750	1.49 (s, 3 H), 0.9-2.0 (m, 10 H), 2.21 and 2.62 (AB q, <i>J</i> = 11 Hz, 2 H), 7.3-7.7 (m, 3 H), 8.0 (m, 1 H)
12c-ex	62-65	3500, 2950, 1680, 1600, 760	1.39 (d, <i>J</i> = 7 Hz, 3 H), 1.53 (s, 3 H), 2.3-2.5 (m, 3 H), 7.2-7.6 (m, 3 H), 8.0 (m, 1 H)
12c-en	98-101	3480, 2970, 1685, 1595, 750	0.81 (d, <i>J</i> = 7 Hz, 3 H), 1.66 (s, 3 H), 1.90 (m, 1 H), 2.66 (m, 1 H), 3.23 (m, 1 H), 7.2-7.6 (m, 3 H), 8.1 (m, 1 H)
12d	107-108.5	3480, 3000, 2950, 1675, 1600, 1200	1.51 (s, 3 H), 2.0-3.3 (m, 4 H), 7.3-7.6 (m, 3 H), 8.1 (m, 1 H)
12e	198	3460, 2950, 1670, 1595, 740, 690	1.53 (s, 3 H), 3.42 and 3.88 (AB q, <i>J</i> = 10 Hz, 2 H), 6.9 (m, 10 H), 7.2-7.8 (m, 3 H), 7.9 (m, 1 H)
12f-ex	185-187	3460, 2950, 1680, 1600, 1450, 740	1.23 (s, 3 H), 1.60 (s, 3 H), 2.33 and 3.66 (AB q, <i>J</i> = 13 Hz, 2 H), 7.2-7.6 (m, 8 H), 8.0-8.2 (m, 1 H)
12f-en	142-143	3460, 2940, 1695, 1600, 740	1.56 (s, 3 H), 1.83 (s, 3 H), 3.00 and 3.20 (AB q, <i>J</i> = 12 Hz, 2 H), 6.8-7.1 (m, 5 H), 7.2-7.8 (m, 4 H)
12g	111-111.5	3450, 1670, 1600, 1295, 760	0.92 (s, 3 H), 1.43 (s, 3 H), 2.16 and 3.00 (AB q, <i>J</i> = 12 Hz, 2 H), 7.2-7.8 (m, 3 H), 8.0 (m, 1 H)
12h	155-157	3450, 1680, 1605, 1295, 750, 700	3.64 (s, 1 H), 3.52 and 3.95 (AB q, <i>J</i> = 10 Hz, 2 H), 6.9-8.0 (m, 14 H)

^a Given in the text. ^b Satisfactory C and H elemental analyses were obtained for all compounds in this table.

Table VI. Properties of β-Diketones 14 and Indenones 18

compd ^b	mp, °C	IR (KBr), cm ⁻¹	¹ H NMR (CDCl ₃), δ
14a	196	<i>a</i>	7.3-7.8 (m, 4 H) ^a
14b	147-149	3420, 2910, 1740, 1685, 1600, 1250	1.36 (s, 3 H), 2.08 and 2.63 (AB q, <i>J</i> = 16 Hz, 2 H), 2.55 (br, 1 H), 1.0-2.0 (m, 10 H), 7.5-7.9 (m, 4 H)
14c-ex	138-139.5	3340, 2960, 1755, 1710, 1055, 780	1.26 (s, 3 H), 1.30 (d, <i>J</i> = 7 Hz, 3 H), 1.70 (dd, <i>J</i> = 4, 17 Hz, 1 H), 2.30 (m, 1 H), 2.32 (dd, <i>J</i> = 8, 17 Hz, 1 H), 7.5-7.9 (m, 4 H)
14c-en	122-125	3500, 2960, 1760, 1695, 1080, 770	1.20 (d, <i>J</i> = 7 Hz, 3 H), 1.33 (s, 3 H), 2.21 (d, <i>J</i> = 6 Hz, 2 H), 2.65 (m, 1 H), 7.6-7.9 (m, 4 H)
14d	133-134	3450, 1750, 1700, 1050, 760	1.27 (s, 3 H), 1.9-2.8 (m, 4 H), 7.4-7.9 (m, 4 H)
14e	220-222	3400, 1745, 1705, 1100	1.36 (s, 3 H), 3.08 (s, 2 H), 6.75 (m, 1 H), 7.1-7.9 (m, 13 H)
14f-ex	177-178	3450, 1750, 1690, 1285, 755	1.13 (s, 3 H), 1.30 (s, 3 H), 2.41 and 3.43 (AB q, <i>J</i> = 16 Hz, 2 H), 7.4-7.9 (m, 9 H)
14f-en	197-198	3510, 1750, 1690, 1260	1.53 (s, 3 H), 1.61 (s, 3 H), 2.28 and 2.75 (AB q, <i>J</i> = 15 Hz, 2 H), 6.13 (m, 1 H), 7.2-7.7 (m, 8 H)
18g	186-187	2990, 1740, 1680, 1375, 730	1.56 (s, 6 H), 2.86 (s, 2 H), 7.4-7.8 (m, 4 H)
18h	228-229	1740, 1690, 1370, 770, 700	3.63 (s, 2 H), 7.0 (m, 1 H), 7.2-7.5 (m, 12 H), 7.7 (m, 1 H)

^a Given in the text. ^b Satisfactory C and H elemental analyses were obtained for all compounds in this table.

Table VII. Properties of β-Alkoxy Enone 15

compd ^c	mp, °C	IR (KBr), cm ⁻¹	¹ H NMR (CDCl ₃), δ
15a	155-156	<i>b</i>	7.3-8.0 (m, 4 H) ^b
15b	178 ^a	3340, 2920, 1660, 1625, 1590, 960	1.56 (s, 3 H), 0.9-2.2 (m, 10 H), 4.55 (s, 2 H), 7.2-7.8 (m, 4 H)
15c-ex	170 ^a	3260, 2950, 1660, 1620, 1595, 955	1.45 (d, <i>J</i> = 7 Hz, 3 H), 1.75 (s, 3 H), 2.65 (m, 1 H), 4.2-4.8 (m, 2 H), 7.2-7.8 (m, 4 H)
15c-en	164-166	3360, 2960, 1665, 1625, 1595, 1215	0.76 (d, <i>J</i> = 7 Hz, 3 H), 1.62 (s, 3 H), 2.94 (m, 1 H), 4.16 (d, <i>J</i> = 8 Hz, 1 H), 5.00 (dd, <i>J</i> = 4, 8 Hz, 1 H), 7.2-7.8 (m, 4 H)
15d	177-178	3350, 1660, 1620, 1595, 1570, 1390	1.59 (s, 3 H), 1.93 (dd, <i>J</i> = 8, 13 Hz, 1 H), 2.83 (dd, <i>J</i> = 5, 13 Hz, 1 H), 4.3-5.0 (m, 1 H), 7.2-7.8 (m, 4 H)
15q	202.5-203	3260, 1640, 1630, 1590, 1170, 1160	0.98 (s, 3 H), 1.57 (s, 3 H), 4.04 and 4.63 (AB q, <i>J</i> = 7 Hz, 2 H), 5.61 (s, 1 H), 7.3-8.0 (m, 4 H)

^a Sublimed. ^b Given in the text. ^c Satisfactory C and H elemental analyses were obtained for all compounds in this table.

column chromatography gave 13a (8 mg, 10%), 14c-en (45 mg, 45%), and 15c-en (12 mg, 12%).

Irradiation of 11d in the Presence of Dimethyl Fumarate. A solution containing 11d (270 mg) and dimethyl fumarate (250 mg) in benzene-*t*-BuOH (1:1, 25 mL) was irradiated for 3 h. After removal of the solvent, the resulting residue was chromatographed over silica gel. The products were 12d (65 mg, 24%), 13a (11 mg, 4%), 6-ethyl-9-methyl-7α,8β-bis(methoxycarbonyl)-6,7,8,9-tetrahydro-6α,9α-epoxybenzocyclooctene-5,10-dione (17a; 72 mg, 16%)

and 6-ethyl-9-methyl-7β,8α-bis(methoxycarbonyl)-6,7,8,9-tetrahydro-6α,9α-epoxybenzocyclooctene-5,10-dione (17b; 68 mg, 15%).

17a: mp 76-78 °C; IR (KBr) 1740, 1735, 1690, 1680, 1440 cm⁻¹; ¹H NMR (CDCl₃) δ 1.22 (t, *J* = 6 Hz, 3 H), 1.44 (s, 3 H), 2.55 (m, 2 H), 3.45 and 3.65 (AB q, *J* = 7 Hz, 2 H), 3.65 (s, 3 H), 3.88 (s, 3 H), 7.5-8.0 (m, 4 H). Anal. Calcd for C₁₉H₂₀O₇: C, 66.27; H, 5.85. Found: C, 66.09; H, 5.77.

17b: mp 98-99 °C; IR (KBr) 1735, 1695, 1685, 1590, 1440 cm⁻¹; ¹H NMR (CDCl₃) δ 1.12 (t, *J* = 6 Hz, 3 H), 1.72 (s, 3 H), 2.44 (m,

Table VIII. Yields and Properties of 38

compd ^b	yield, %	mp, °C	IR (KBr), cm ⁻¹	¹ H NMR (CDCl ₃), ^a δ
38a	78	134-135	2960, 1750, 1740, 1710, 1235	2.12 (s, 2 H), 7.6-7.8 (m, 4 H)
38b	73	185-186	2920, 1755, 1740, 1715, 1240	1.0-2.1 (m, 11 H), 2.60 (d, <i>J</i> = 16 Hz, 1 H), 7.4-7.8 (m, 4 H)
38c-ex	79	162-162.5	1760, 1735, 1715, 1245	1.9 (m, 1 H), 2.3 (m, 1 H), 2.6 (m, 1 H), 7.5-7.9 (m, 4 H)
38c-en	84	143-144	1750, 1735, 1705, 1240	2.0-2.2 (m, 2 H), 3.3 (m, 1 H), 7.5-8.0 (m, 4 H)
38d	63	109-111	1760, 1730, 1710, 1240	1.7-2.2 (m, 4 H), 7.3-7.9 (m, 4 H)
38e	85	255-257	1760, 1745, 1720, 1235	2.96 and 3.23 (AB q, <i>J</i> = 16 Hz, 2 H), 7.2-7.8 (m, 14 H)
38f-ex	68	179-180	1760, 1750, 1715, 1240	2.35 and 3.22 (AB q, <i>J</i> = 17 Hz, 2 H), 7.2-7.8 (m, 9 H)
38f-en	72	214-215	1760, 1745, 1715, 1240	2.27 and 3.67 (AB q, <i>J</i> = 16 Hz, 2 H), 5.9 (m, 1 H), 7.0-7.8 (m, 8 H)

^a Data of methyl protons are shown in Figure 4. ^b Satisfactory C and H analyses were obtained for all compounds in this table.

2 H), 3.54 and 3.77 (AB q, *J* = 7 Hz, 2 H), 3.65 (s, 3 H), 3.77 (s, 3 H), 7.5-8.0 (m, 4 H). Anal. Calcd for C₁₉H₂₀O₇: C, 66.27; H, 5.85. Found: C, 66.43; H, 5.99.

The C-9 methyl protons of 17b appeared at lower field than those of 17a presumably because of the proximity of the C-8α methoxycarbonyl group, while the methylene protons at the C-6 ethyl group of 17a appeared at lower field than those of 17b.

Reductive Acetylation of the β-Alkoxy Enone 15g. A solution of 15g (70 mg), anhydrous NaOAc (130 mg), and Zn dust (700 mg) in 5 mL of acetic anhydride was refluxed for 30 min. The reaction mixture was poured into 50 mL of saturated NaHCO₃ solution and extracted with two portions of CH₂Cl₂ (50 mL), and the organic extracts were washed with water before being dried (Na₂SO₄). Removal of the solvent afforded crude product, which was purified by silica gel short column, giving 16g (50 mg, 68%).

8-Acetoxy-3,3-dimethyl-2,3-dihydronaphthaleno[1,2-*b*]furan (16g): colorless oil; IR (CCl₄) 2940, 1760, 1620, 1360, 1190, 1135, 755 cm⁻¹; ¹H NMR (CDCl₃) δ 1.60 (s, 6 H), 2.42 (s, 3 H), 4.37 (s, 2 H), 6.91 (s, 1 H), 7.2-8.1 (m, 4 H). Anal. Calcd for C₁₆H₁₆O₃: C, 74.98; H, 6.29. Found: C, 74.68; H, 6.18.

General Procedure for Acetylation of the β-Diketones 14. A solution of 14 (100 mg) in 20 mL of acetic anhydride was cooled to -20 °C, 3 drops of HClO₄ were added cautiously, and then the mixture was immediately poured into 100 mL of ice-water. The reaction mixture was extracted with two portions of CH₂Cl₂, and the organic extracts were washed with water. Removal of the solvent afforded a yellow oil, which was separated by column chromatography, giving 35. Yields and physical properties are summarized in Table VIII.

Acetylation of the Cyclobutanol 12a. A solution of 12a (480 mg) in 30 mL of acetic anhydride was cooled to -20 °C, 3 drops of HClO₄ were added cautiously, and the mixture was immediately poured into 200 mL of ice-water. The reaction mixture was extracted with two portions of CH₂Cl₂, and the organic extract was washed with water. After removal of the solvent, the residual oil was chromatographed on silica gel column, giving colorless crystals of 1-acetoxy-3,10,10-trimethyl-1,2,3,4-tetrahydro-2,3-epoxy-1,2-ethanonaphthalen-4-one (34a): 167 mg (30%); mp 114-115 °C; IR (KBr) 2960, 1760 (ester C=O), 1700 (ketone C=O), 1380,

1220, 1035 cm⁻¹; ¹H NMR (CDCl₃) δ 0.85 (s, 3 H), 1.48 (s, 3 H), 1.52 (s, 3 H), 2.05 (s, 3 H), 2.10 and 2.86 (AB q, *J* = 12 Hz, 2 H), 7.0-7.6 (m, 3 H), 8.0-8.2 (m, 1 H). Anal. Calcd for C₁₇H₁₈O₄: C, 71.31; H, 6.34. Found: C, 71.22; H, 6.30.

Irradiation of 34a in Benzene Solution. A benzene solution of 34a (100 mg) was irradiated for 3 h. After removal of the solvent, the resulting residue was separated by column chromatography on silica gel. The major product was the β-diketone acetate 35a (52 mg, 52%), and small amount (13 mg) of unidentified product was also obtained.

Quantum Yield Determination. Valerophenone actinometry was used for quantum yield determination. The 313-nm line was isolated with a filter solution containing 0.002 M K₂CrO₄ in a 1% aqueous solution of K₂CO₃. The degree of the reaction was determined by GC analysis relative to known concentration of alkane internal standard.

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Registry No. 10a, 81847-25-8; 10b, 81847-26-9; 10c, 2397-61-7; 10d, 2589-56-2; 10e, 81847-27-0; 10f, 81847-28-1; 10g, 73377-70-5; 10h, 81847-29-2; 11a, 73645-14-4; 11b, 81847-30-5; 11c, 81856-92-0; 11d, 73377-87-4; 11e, 73645-15-5; 11f, 81847-31-6; 11f', 81873-93-0; 11g, 73645-16-6; 11h, 74954-83-9; 11i, 53948-58-6; 11j, 74954-87-3; 12a, 81873-94-1; 12b, 81847-32-7; 12c-ex, 81847-33-8; 12c-en, 81873-95-2; 12d, 81847-34-9; 12e, 73645-22-4; 12f-ex, 81847-35-0; 12f-en, 81873-96-3; 12g, 73645-23-5; 12h, 74954-90-8; 13a, 483-55-6; 13b, 83-72-7; 14a, 81847-36-1; 14b, 81847-37-2; 14c-ex, 81847-38-3; 14c-en, 81873-97-4; 14d, 81847-39-4; 14e, 81847-40-7; 14f-ex, 81938-68-3; 14f-en, 81847-41-8; 14g, 81847-42-9; 14h, 81847-43-0; 15a, 73645-24-6; 15b, 81847-44-1; 15c-ex, 81847-45-2; 15c-en, 81847-46-3; 15d, 81847-47-4; 15g, 73645-25-7; 16a, 74954-81-7; 16g, 81847-48-5; 17a, 81847-49-6; 17b, 81873-98-5; 18g, 73645-28-0; 18h, 74954-86-2; 31i, 81856-93-1; 31j, 81856-94-2; 34a, 81847-50-9; 35a, 81847-51-0; 35b, 81847-52-1; 35c-ex, 81847-53-2; 35c-en, 81873-99-6; 35d, 81847-54-3; 35e, 81847-55-4; 35f-ex, 81847-56-5; 35f-en, 81874-00-2; dimethyl fumarate, 624-49-7.