

Reaction of 4-Butyl-1,2,4-triazoline-3,5-dione with 1,3,5-Trimethoxybenzene. The reaction was carried out as above with the 4-phenyl compound. After a 5-h reaction time, the solvent was removed under vacuum to give a resinous residue. Addition of ether induced crystallization. The product was filtered, washed, and recrystallized from ethanol at -10°C to give a 68% yield of product, mp $156\text{--}157^{\circ}\text{C}$. Ethanol of crystallization was removed by heating to 130°C for 30 min. $^1\text{H NMR}$ (CDCl_3) δ 0.95 (3 H, t), 1.2-1.9 (4 H, m), 3.59 (2 H, t), 3.79 (6 H, s), 3.81 (3 H, s), 6.13 (2 H, s), 7.99 (1 H, br s); $^{13}\text{C NMR}$, (CDCl_3) δ 13.7, 19.7, 30.0, and 39.2 (*n*-butyl), 55.6 (4- CH_3O), 56.1 (2,6- CH_3O), 91.1, 106.3, 158.5, and 162.4 (C-3, C-1, C-2, and C-4 of aryl ring), 153.6 and 155.7 (C-3 and C-5 of urazole).

Anal. Calcd $\text{C}_{15}\text{H}_{21}\text{N}_3\text{O}_5$: C, 55.71; H, 6.55; N, 13.00. Found: C, 55.72; H, 6.75; N, 12.80.

Acknowledgment. I express my appreciation to the Monsanto Chemical Co. for purchase of a Perkin-Elmer 340 spectrometer used in the kinetic studies.

Registry No. 1a, 84751-99-5; 1b, 84752-00-1; 2a, 84752-01-2; 1,4-dimethoxybenzene-4-phenyl-1,2,4-triazoline-3,5-dione complex, 84752-02-3; 4-phenyl-1,2,4-triazoline-3,5-dione, 4233-33-4; 4-butyl-1,2,4-triazoline-3,5-dione, 13482-57-0; 1,3,5-trimethoxybenzene, 621-23-8; 1,3-dimethoxybenzene, 151-10-0; anisole, 100-66-3.

Photochemistry of Epoxyquinone. 5. Photoinduced Cycloadditions of Epoxynaphthoquinone to Aldehydes, Ketones, and Oxygen^{1,2}

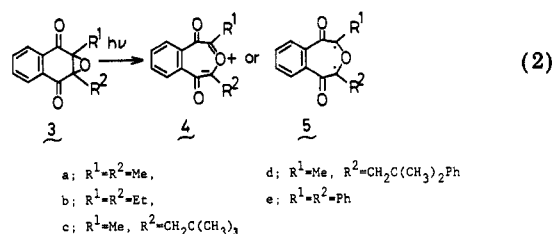
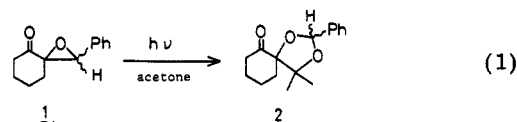
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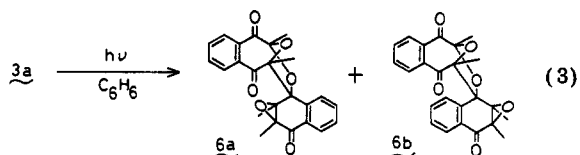
Received November 17, 1981

Irradiation of a benzene solution of 2,3-dihydro-2,3-dimethyl-2,3-epoxy-1,4-naphthoquinone (**3a**) in the presence of aldehydes gives the primary 1,3-dioxolane adducts in good yields. Upon further irradiation, the primary adducts undergo photorearrangement to give alkylidenephthalides. A similar photocycloaddition reaction of **3a** with aliphatic ketones was realized by their use as the reaction medium. When irradiated in the presence of oxygen in benzene, **3a** was converted into 3-acetyl-3-acetoxypthalide and 3-acetoxy-3-methylisochroman-1,4-dione presumably via the reaction of singlet oxygen with a carbonyl ylide, **4a**. In contrast to 2,3-dialkylepoxynaphthoquinones **3a-d**, the photoinduced cycloaddition of 2,3-dihydro-2,3-diphenyl-1,4-naphthoquinone (**3e**) to carbonyl compounds did not occur. The photoinduced cycloadditions of epoxynaphthoquinones to carbonyl compounds are believed to be HOMO-controlled reactions on the basis of substituent effects at the 2- and 3-positions of epoxy-naphthoquinones and at the para position of the dipolarophiles, namely, aromatic aldehydes.

Ring-opening reactions at C-C bonds of oxiranes have attracted considerable interest from both synthetic and mechanistic standpoints.^{3,4} Especially, 1,3-dipolar cycloaddition of carbonyl ylides to carbonyl compounds constitutes among the most convenient methods for the synthesis of 1,3-dioxolane compounds. While several examples of 1,3-dipolar cycloaddition reactions of thermally generated carbonyl ylides with less volatile carbonyl compounds can be found in literature,⁵ relatively little is known about the cycloaddition of photogenerated carbonyl ylides to carbonyl compounds. In one system, Pête et al. have recently described the photocycloaddition reaction of the α,β -epoxy ketone **1** to acetone leading to the formation of the 1,3-dioxolane **2**⁶ (eq 1). Recently, we have reported that irradiation of several epoxynaphthoquinones gives carbonyl ylides **4** or 1,3-diradical **5** (eq 2), which may be trapped by alkenes or dipolarophiles such as 2-norbornene and *N*-phenylmaleimide.⁷ When irradiated in a benzene



solution (0.1 M) in the absence of 1,3-dipolarophile, 2,3-dimethyl-2,3-dihydro-2,3-epoxy-1,4-naphthoquinone (**3a**) is converted into dimers **6a** and **6b** (eq 3) in good yields



via the cycloaddition of **4a** or **5a** to the carbonyl group of another molecule of **3a**.¹ This result prompted to investigate the possibility of trapping of **4** or **5** with simple aldehydes and ketones. In this paper, the photolyses of epoxynaphthoquinones in the presence of various aldehydes and ketones were examined and the 1,3-dipolar cycloadditions of **4** or **5** to aldehydes and ketones as well as

(1) Part 4: Maruyama, K.; Osuka, A. *J. Org. Chem.* 1980, 45, 1898.

(2) For preliminary reports on some aspects of the present study, see: (a) Maruyama, K.; Osuka, A. *Chem. Lett.* 1979, 77. (b) Maruyama, K.; Osuka, A.; Suzuki, H. *Chem. Lett.* 1979, 1477. (c) Maruyama, K.; Osuka, A.; Suzuki, H. *J. Chem. Soc. Chem. Commun.* 1980, 723.

(3) (a) Linn, W. J.; Benson, R. E. *J. Am. Chem. Soc.* 1965, 87, 3657. (b) Ullman, E. F.; Milks, J. E. *Ibid.* 1962, 84, 315; 1964, 86, 3814. (c) Petrellis, P. C.; Dietrich, H.; Meyer, E.; Griffin, G. W. *Ibid.* 1967, 89, 1967. (d) Do-Minh, T.; Trozolo, A. M.; Griffin, G. W. *Ibid.* 1970, 92, 1402. (e) Huisgen, R.; *Angew. Chem., Int. Ed. Engl.* 1977, 16, 572 and references cited therein.

(4) (a) Houk, K. N.; Sims, J.; Duke, R. E., Jr.; Stroziew, R. W.; George, J. K. *J. Am. Chem. Soc.* 1973, 95, 7287. (b) Houk, K. N.; Sims, J.; Watts, C. R.; Luskus, L. J. *Ibid.* 1973, 95, 7301. (c) Bigot, B.; Sevin, A.; Devaquet, A. *Ibid.* 1979, 101, 1095; 1979, 101, 1101.

(5) Robert, A.; Pommeret, J. J.; Foucaud, A. *Tetrahedron* 1972, 28, 2085.

(6) Muzart, J.; Pête, J. *ep. Tetrahedron Lett.* 1977, 303.

(7) Arakawa, S. *J. Org. Chem.* 1977, 42, 3800.

Table I. Photoinduced Cycloaddition of 3a to Aldehydes

aldehyde	R	total yields, ^a %	8/9 ^b	products (mp, °C)
7a	Me	71 (91) ^c	1.7	8a (98), 9a (75-76.5)
7b	Et	75	1.9	8b (92-93), 9b (80-81)
7c	Pr	65	1.8	8c (oil), 9c (82-84)
7d	<i>i</i> -Pr	60	1.0	8d (94), 9d (90-91)
7e	(Et) ₂ CH	70	1.2	8e (96-97), 9e (85-87)
7f	PhCH ₂	59	2.0	8f (125-126), 9f (141-142)
7g	Ph ₂ CH	46	1.4	8g (121-122), 9g (167-168)
7h	CH ₃ (CH ₂) ₁₀	29	<i>d</i>	8h (100-101)
7i	<i>p</i> -NO ₂ Ph	86	0.33	8i (165-166), 9i (187)
7j	<i>p</i> -MeOPh	70	0.23	8j (148-149), 9j (152-153)
7k	<i>p</i> -MePh	76	0.37	8k (130-131), 9k (158-159)
7l	Ph	82	0.35	8l (132-133), 9l (146-147)
7m	<i>p</i> -ClPh	80	0.65	8m (168-170), 9m (175-176)

^a Isolated yields. ^b Product ratios 8/9 were determined by HPLC. ^c ¹H NMR yield. ^d Not determined.

Table II. ¹H NMR Data of Primary Adducts 8 and 9^a

compd	H ^a	H ^b	H ^c	compd	H ^a	H ^b	H ^c
8a	1.66	1.56	4.00 (q)	9a	1.66	1.48	4.32 (q)
8b	1.66	1.56	3.72 (dd)	9b	1.66	1.48	4.00 (dd)
8c	1.65	1.56	3.85 (dd)	9c	1.65	1.48	4.10 (dd)
8d	1.64	1.60	3.48 (d)	9d	1.64	1.55	3.62 (d)
8e	1.64	1.62	3.78 (d)	9e	1.62	1.53	3.96 (d)
8f	1.70	1.58	4.18 (dd)	9f	1.82	1.62	4.50 (dd)
8g	1.76	1.19	4.82 (d)	9g	1.70	1.24	5.24 (d)
8h	1.62	1.52	4.10 (dd)				
8i	1.87	1.80	5.08 (s)	9i	1.92	1.14	5.28 (s)
8j	1.85	1.74	5.00 (s)	9j	1.88	1.14	5.16 (s)
8k	1.83	1.70	5.08 (s)	9k	1.88	1.12	5.20 (s)
8l	1.84	1.72	5.06 (s)	9l	1.89	1.12	5.20 (s)
8m	1.84	1.72	5.03 (s)	9m	1.89	1.14	5.22 (s)

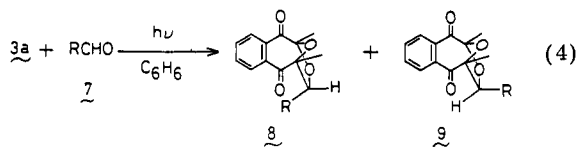
^a The values are given in δ units. For the data of H^d, see Table V.

the photoinduced oxygenation of 3a are reported.

Results and Discussion

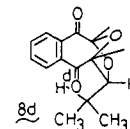
Photoinduced Cycloaddition of 3a to Aldehydes.

Irradiation of a benzene solution of 3a (0.012 M) in the presence of acetaldehyde 7a (0.15 M) with radiation of wavelength above 300 nm for 30 min afforded a 1.7:1 mixture of 1,3-dioxolanes 8a and 9a (eq 4) in high yield



(92% by ¹H NMR). The products were separated by silica gel chromatography (8a, 49%; 9a, 22%) and characterized by their spectral data and elemental analyses (see Experimental Section). Similar reactions with aliphatic aldehydes 7b-h and aromatic aldehydes 7i-m gave 1,3-dioxolanes 8 and 9 in moderate to high yields, and the results are summarized in Tables I and II. The b-methyl protons of 9i-m are characterized by a marked upfield shift (δ 1.12-1.14) resulting from shielding by the aromatic ring. In the ¹H NMR spectra of 9i-m, the chemical shifts observed for H^c protons were lower relative to those of 8i-m without exception, probably due to the proximity of carbonyl group to the H_c proton. On the basis of these observations, 8a-g and 9a-g were assigned to be endo and exo structures, respectively, by the comparison of the chemical shifts of H_c methine protons. Consistent with this assignment is the fact that b-methyl protons of 9a-e

were slightly shielded by steric repulsion by the *vicinal* alkyl groups compared with those of 8a-e. Further, the H_d protons of 8d are considerably shielded at δ 1.50 by the



aromatic rings, presumably because of restricted rotation of the isopropyl group (compare H_d of 9d at δ 1.96). The ratios of 8 to 9 (endo/exo) formed in the reaction were readily determined by high-performance LC (HPLC) and are listed in Table I. In the case of aliphatic aldehydes, endo adducts 8 were formed preferentially, while exo adducts 9 were the predominant products in the reaction with aromatic aldehydes. It seems likely that endo approach is more hindered, since endo/exo ratios decreased with increasing bulkiness of the alkyl group of aliphatic aldehydes from 7a to 7e. Therefore, preferential formation of endo adducts 8 in the reaction with aliphatic aldehydes implies two points, that electronic interactions between the 1,3-dipole and alkyl groups of aliphatic aldehydes must be operative in the transition state and that the cycloaddition with aliphatic aldehydes appears to proceed in a concerted fashion,⁸ for if intermediate 10 or 11 interv-

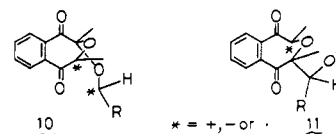


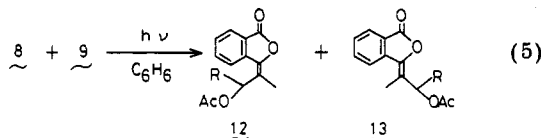
Table III. Relative Rates of Para-Substituted Benzaldehydes toward 3a

aldehyde	substituent	rel rate
7i	NO ₂	103
7m	Cl	44
7l	H	30
7k	CH ₃	17
7j	MeO	4.0
7c		1

ened, free rotation around the C–O bond would be expected to take place prior to ring closure, probably resulting in the preferential formation of less hindered *exo* adducts 9. On the other hand, preferential formation of *exo* adducts in the reaction with aromatic aldehydes may be ascribed to either critical steric encumbrance by buttressing phenyl groups or a stepwise mechanism in which the intermediate 10 would be better stabilized by the aromatic rings.⁵ Kobuke and Fueno have reported that a methyl group shows a greater tendency toward *endo* orientation in Diels–Alder reactions with cyclopentadiene than most of electron-accepting polar groups such as CHO, CN, and COOH.⁹ Intermolecular dispersion forces were advanced to explain the origin of the *endo*-orientating ability of a methyl substituent, but a definitive explanation remains to be presented. It is reasonable to assume that electronic interactions between 4a or 5a and the alkyl groups of aliphatic aldehydes are similar in magnitude. The interplay of steric factors and ill-defined electronic factors would determine the *endo/exo* ratio.

The relative rates for the reaction of carbonyl ylide 4a or 1,3-diradical 5a with para-substituted benzaldehydes 7i–m were determined by using butyraldehyde 7c as a probe. A benzene solution of 3a, 7c, and aromatic aldehyde was irradiated for a short time such that the relative ratio of two aldehydes did not change significantly from the initial ratio. Product yields were determined by HPLC.¹⁰ The results in Table III show clearly that aromatic aldehydes are more reactive than butyraldehyde 7c and that electron-attracting substituents in the para position of aromatic aldehydes accelerate the reaction.¹¹

The primary 1,3-dioxolane adducts 8 and 9 proved photolabile and upon prolonged irradiation gave a mixture of alkylidene phthalides 12 and 13 in high yields^{2b} (eq 5).

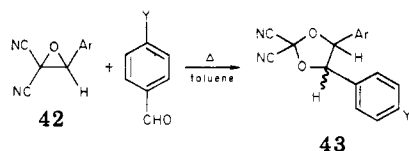


(8) In the photoinduced cycloaddition of 3a to *trans*- or *cis*-2-butene, the stereochemistry of olefin was completed retained in the cycloadducts, suggesting that the addition proceeded via a concerted 4 + 2 addition.

(9) (a) Kobuke, Y.; Fueno, T.; Furukawa, J. *J. Am. Chem. Soc.* 1970, 92, 6548. (b) Kobuke, Y.; Sugimoto, T.; Furukawa, J. *Ibid.* 1972, 94, 3633.

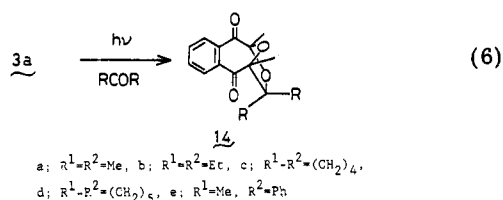
(10) In the HPLC chart, 1,3-dioxolanes 8c and 9c derived from the reaction of 3a with butyraldehyde eluted at 2.00 and 2.30 min, respectively, 3a at 2.60 min, and 1,3-dioxolanes 8i–m and 9i–m at later than 4 min.

(11) In ref 5 Roberts et al. have also reported the order of decreasing relative reactivity, Y; NO₂ > H > MeO, in the thermal cycloaddition reactions of 1,1-dicyano-2-aryloxirane with para-substituted benzaldehydes.



(12) Lewis, F. D.; Magyar, J. G. *J. Org. Chem.* 1972, 37, 2102.

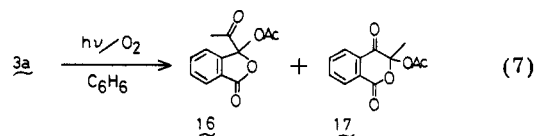
Photoinduced Cycloaddition of 3a to Ketones. Solutions of 3a in the neat ketones were employed in the photochemical studies of aliphatic series, since such ketones are much less reactive toward 4a or 5a than the carbonyl group of 3a. Irradiation of an acetone solution of 3a (82.5 mM) gave the 1,3-dioxolane adduct 14a in 23% yield (eq 6), in addition to dimers 6a (26%) and 6b (13%),



indicating that acetone is only 3.6×10^{-3} times as reactive as 3a. When irradiated in a dilute acetone solution, 3a was converted to 14a in 85% yield. Similar 1,3-dioxolanes 14b–d were obtained upon irradiation of 3a in solution in various other ketones (Table IV). In these photolyses, radiation of wavelength below 341 nm was almost all absorbed by ketones used as the solvent. It seems likely that for the most part the excited ketones not only transfer energy to 3a but also undergo photochemical reactions such as α cleavage which leads to products which contaminate the reaction mixture (runs 3 and 4 in Table IV). In fact, 14b was obtained in a higher yield (53%) when the irradiation was conducted with radiation filtered through an acetone solution.

On the other hand, acetophenone 15 was found to be more reactive toward 4a or 5a to the extent that irradiation of a benzene solution of 3a (82.5 mM) and 15 (138 mM) gave the 1,3-dioxolane 14e in 26% yield and the dimers 6a and 6b in 40% and 25% yields, respectively. The ¹H NMR spectrum of 14e displays three methyl singlets at δ 1.08, 1.48, and 1.86, which indicates that the configuration of the phenyl group in 14e is *exo*. Predominant formation of the *exo*-phenyl adduct 14e may be ascribed to the conjunction of *endo* selectivity of the methyl substituent acting in concert with the steric bulkiness of the phenyl group. It is of interest to compare the relative reactivity of ketones toward 4a or 5a by using the dimerization of 3a as a probe. The results observed are listed in Table IV. Aromatic ketones 3a and 15 react 10² times faster than aliphatic ketones, and, curiously, cyclohexanone is 10 times as reactive as acetone, 3-pentanone, and cyclopentanone.

Photoinduced Oxygenation of 3a. A dilute benzene solution of 3a (4 mM) was saturated with oxygen and irradiated through a Pyrex filter for 30 min while a stream of oxygen was passed through the solution. 3-Acetyl-3-acetoxypthalide (16, 43%) and 3-acetoxy-3-methylisochroman-1,4-dione (17, 13%) were isolated as major products (eq 7) upon chromatographing the products on

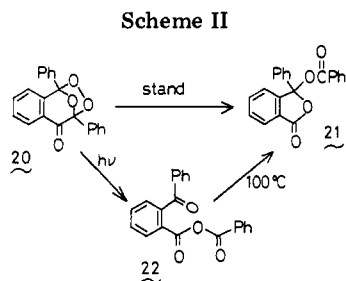
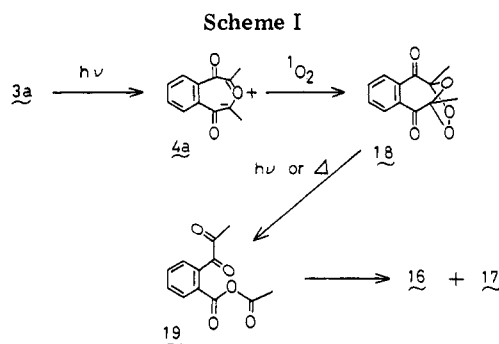


a Fluorisil column.^{2c} Irradiation of a degassed benzene solution of 3a under similar conditions gave no products identified as 16 and 17. The effects of Rose Bengal and β -carotene suggest that singlet oxygen is involved in the photooxygenation of 3a.^{2c} A tentative mechanism for the reaction is shown in Scheme I. Singlet oxygen adds to the carbonyl ylide 4a or 1,3-diradical 5a in a manner analogous to that observed for reactive dipolarophiles. The ozonide 18 thus formed undergoes a Baeyer–Villiger-type rear-

Table IV. Photoinduced Cycloaddition of 3a to Ketones

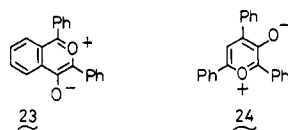
run	ketone	concn, ^a mM	irradn time, h	product distribution, ^b %		rel reactivity to 3a (× 10 ³)
				14 (mp, °C)	dimers ^c	
1	acetone	82.5	12	23; 14a (86.5-87)	39	3.6
2	acetone	8.25	1	85; 14a		
3	2-pentanone	40	1.5	12; 14b (55-57)	12	4.2
4	2-pentanone	10	1	17; 14b		
5	2-pentanone	10	22 ^d	53; 14b		
6	cyclopentanone	82.5	12	19; 14c (58-59)	51	2.7
7	cyclopentanone	8.25	1	69; 14c	18	2.8
8	cyclohexanone	82.5	12	57; 14d (85)	21	23
9	cyclohexanone	8.25	1	78; 14d		
10	acetophenone ^e	82.5	2.5	26; 14e (123-125)	65	240

^a Concentration of 3a. ^b Isolated yields based on the consumed amount of 3a. ^c Sum of the yields of dimers 6a + 6b. ^d Irradiation was carried out through an acetone filter. ^e A benzene solution of acetophenone (133 mM) was irradiated.



rangement to give the diketo anhydride 19 which finally undergoes isomerization to 16 and 17. Criegee et al. have found that closely related ozonide 20, which is known as one of the extremely stable ozonides, decomposes slowly to give 3-(benzoyloxy)-3-phenylphthalide (21,¹³ Scheme II). Ullman and Henderson have reported that 20 readily undergoes photorearrangement to 22 and finally gives the isomerized product 21.¹⁴

In recent years, reports have appeared in the literature that singlet oxygen will behave as a dipolarophile toward ylides,¹⁵ diazoalkanes,¹⁶ and nitrones;¹⁷ however, the oxygenation of carbonyl ylides has been limited to stable pyrylium oxides such as the diphenylbenzopyrylium oxide 23¹⁴ and 2,4,6-triphenylpyrylium oxide 24.¹⁸ It is of in-



(13) Criegee, R.; de Bruyn, P.; Lohaus, G. L. *Justus Liebigs Ann Chem.* 1953, 583, 19.

(14) Ullman, E. F.; Henderson, W. A., Jr. *J. Am. Chem. Soc.* 1967, 89, 4390.

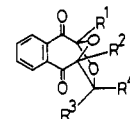
(15) (a) Padwa, A.; Vega, E. *J. Org. Chem.* 1975, 40, 175. (b) Ando, W.; Kohmoto, S.; Nishizawa, K. *J. Chem. Soc., Chem. Commun.* 1978, 894, (c) Bhat, V.; George, M. V. *J. Org. Chem.* 1977, 44, 3288.

(16) Higley, D. P.; Murray, R. W. *J. Am. Chem. Soc.* 1974, 96, 3330.

(17) Foote, C. S.; Ching, T. Y. *Tetrahedron Lett.* 1975, 2771.

terest to note that this photooxygenation proceeds via a photochemically generated transient carbonyl ylide.

Effects of Substituents at 2,3-Positions of Epoxy-naphthoquinones. The effect of substituents at 2,3-positions of epoxy-naphthoquinones was investigated by irradiating epoxy-naphthoquinones 3b-e in the presence of aldehydes and ketones. Irradiation of a benzene solution of 3b (0.01 M) in the presence of acetaldehyde (0.2 M) for 1 h gave 1,3-dioxolanes 25 (32%) and 26 (24%), together



	R ¹	R ²	R ³	R ⁴
25	Et	Et	Me	H
26	Et	Et	H	Me
28	Me	CH ₂ C(CH ₃) ₃	Me	H
29	Me	CH ₂ C(CH ₃) ₃	H	Me
30	CH ₂ C(CH ₃) ₃	Me	Me	H
31	CH ₂ C(CH ₃) ₃	Me	H	Me
32	Et	Et	Me	Me
33	Me	CH ₂ C(CH ₃) ₃	Me	Me
34	CH ₂ C(CH ₃) ₃	Me	Me	Me
35	Me	CH ₂ C(CH ₃) ₂ Ph	Me	Me
36	CH ₂ C(CH ₃) ₂ Ph	Me	Me	Me

with 2-ethyl-3-hydroxy-1,4-naphthoquinone (27, 4%). The latter product suggests that a Norrish Type II photoprocess has accompanied the generation of 4b or 5b.¹⁹ Irradiation of a benzene solution of 3c and acetaldehyde gave four 1,3-dioxolanes, 28 (12%), 29 (9%), 30 (26%), and 31 (10%).

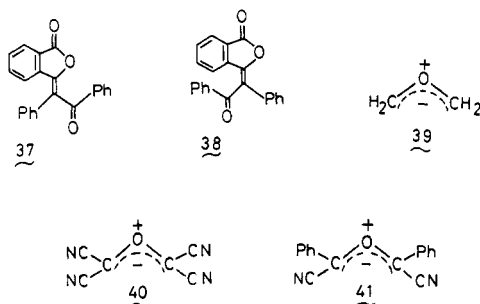
Irradiation of an acetone solution of 3b (0.01 M), however, produced a complex mixture from which a low yield (7%) of 1,3-dioxolane 32 was isolated, in addition to 27 (3%). The competitive Norrish Type II photoreaction of 3b and the low reactivity of acetone as a dipolarophile for carbonyl ylides or 1,3-diradicals might be responsible for the poor yield of 32. When irradiated in acetone, epoxy-naphthoquinone 3c, which has no γ -hydrogen atom, was clearly converted into two 1,3-dioxolanes, 33 (39%) and 34 (41%). Similarly, irradiation of an acetone solution of 3d gave the corresponding 1,3-dioxolanes 35 (23%) and 36 (12%).

In contrast to 2,3-dialkyl-substituted epoxy-naphthoquinones, no 1,3-dioxolanes are formed when 2,3-diphenyl-2,3-dihydro-2,3-epoxy-1,4-naphthoquinone (3e) is irradiated in acetone or in the presence of acetaldehyde (0.2 M) in benzene. Irradiation of a benzene-methanol

(18) Wasserman, H. H.; Pavia, D. L. *J. Chem. Soc., Chem. Commun.* 1970, 1459.

(19) Maruyama, K.; Osuka, A.; Suzuki, H. *J. Chem. Soc., Chem. Commun.* 1980, 323.

(40:1) solution of **3e** containing Rose Bengal and continuously saturated with oxygen affords no oxygenated products. In all cases, only a slow photoisomerization to alkylidene-phthalides **37** and **38** takes place.²⁰ Therefore,



the carbonyl ylide **4e** or 1,3-diradical **5e** derived from **3e** does not react with electron-deficient 1,3-dipolarophiles such as aldehydes, ketones, and singlet oxygen, in contrast to alkenes such as 2-norbornene and *N*-phenylmaleimide, where clean cycloaddition reactions are observed.⁷

Recently, Houk et al. have suggested that the frontier orbital energies of 1,3-dipoles are dominant factors in the reactivities toward various dipolarophiles.^{4a,b} On the basis of the estimated frontier orbital energies, the parent carbonyl ylide **39** should be a typical HOMO-controlled dipole (the interaction of the dipole HOMO with the dipolarophile LUMO is greatest),^{4a} but the tetracyano compound **40** has considerably lowered frontier orbital energies and reacts most readily with electron-rich dipolarophiles^{3a} (LUMO-controlled dipole; the interaction of the dipole LUMO with the dipolarophile HOMO is greatest). The less electron-deficient carbonyl ylide **41** formed from 2,3-dicyano-2,3-diphenyloxirane is reactive with both electron-deficient and electron-rich dipolarophiles (HOMO-, LUMO-controlled dipole).²¹

It seems likely that carbonyl ylides **4a–d** or 1,3-diradicals **5a–d** generated from 2,3-dialkyl-substituted epoxy-naphthoquinones are best classified as HOMO/LUMO-controlled dipoles, since **4a–d** or **5a–d** react with both electron-deficient and electron-rich dipolarophiles. On the other hand, the HOMO orbital of diphenyl compound **4e** or **5e** appears to have a much lower energy and fails to interact significantly with the LUMO orbital of carbonyl compounds. In the present cycloaddition reactions of **4a** or **5a** with carbonyl compounds, electron-attracting substituents at the para positions of aromatic aldehydes accelerate the rate of cycloaddition, and aromatic carbonyl compounds are more reactive than the corresponding aliphatic carbonyl compounds; e.g., benzaldehyde reacts 30–40 times faster than acetaldehyde, and acetophenone reacts 60–70 times faster than acetone. These results indicate that the cycloaddition reactions of **4a** or **5a** with carbonyl compounds are HOMO controlled.

In summary, irradiation of 2,3-dialkyl-substituted epoxy-naphthoquinones in the presence of aldehydes or ketones leads to the formation of a new class of tricyclic 1,3-dioxolanes, which, in turn, can be transformed into alkylidene phthalides in good yields. The cycloaddition of the carbonyl ylide **4** or 1,3-diradical **5** to aldehydes or ketones may be designated as a HOMO-controlled reaction, but the reaction fails to occur in the case of the diphenyl-substituted analogue **4e** or **5e**.

Experimental Section

General Methods. The instruments and procedures were as previously reported.¹

Epoxy-naphthoquinones **3a,b,e** were prepared by the method of Arakawa,⁷ and **3c** and **3d** were prepared by epoxidation of the corresponding 1,4-naphthoquinones with NaOCl/pyridine. The 1,4-naphthoquinones were synthesized by the method of Jacobsen.²²

2-Methyl-3-(2,2-dimethylpropyl)-1,4-naphthoquinone (42): mp 93–94.5 °C; IR (KBr) 2910, 1660, 1600, 1300 cm⁻¹; ¹H NMR (CDCl₃) δ 0.95 (s, 9 H), 2.22 (s, 3 H), 2.71 (s, 2 H), 7.6–7.7 (m, 2 H), 8.1–8.2 (m, 2 H). Anal. Calcd for C₁₆H₁₈: C, 79.31; H, 7.49. Found: C, 79.22; H, 7.53.

2,3-Dihydro-2,3-epoxy-2-methyl-3-(2,2-dimethylpropyl)-1,4-naphthoquinone (3c): mp 113–115 °C; IR (KBr) 2910, 1695, 1600, 1310, 720, 710 cm⁻¹; ¹H NMR (CDCl₃) δ 1.02 (s, 9 H), 1.73 (s, 3 H), 1.72 and 2.70 (AB q, *J* = 14 Hz, 2 H), 7.2–7.6 (m, 2 H), 7.6–7.8 (m, 2 H). Anal. Calcd for C₁₆H₁₈O₃: C, 74.39; H, 7.02. Found: C, 74.52; H, 7.00.

2-Methyl-3-(2-methyl-2-phenylpropyl)-1,4-naphthoquinone (43): mp 77–78 °C; IR (KBr) 2920, 1665, 1655, 1595, 1295, 730, 700 cm⁻¹; ¹H NMR (CDCl₃) δ 1.36 (s, 6 H), 1.67 (s, 3 H), 3.00 (s, 2 H), 7.2–7.4 (m, 5 H), 7.6–7.7 (m, 2 H), 7.9–8.1 (m, 2 H). Anal. Calcd for C₂₁H₂₀: C, 82.86; H, 6.62. Found: C, 82.45; H, 6.71.

2,3-Dihydro-2,3-epoxy-2-methyl-3-(2-methyl-2-phenylpropyl)-1,4-naphthoquinone (3d): mp 113–114.5 °C; IR (KBr) 2950, 1700, 1690, 1600, 1500, 1310, 1290, 940, 720 cm⁻¹; ¹H NMR (CDCl₃) δ 1.43 (s, 3 H), 1.46 (s, 3 H), 1.48 (s, 3 H), 2.13 and 2.93 (AB q, *J* = 14 Hz, 2 H), 7.2–7.6 (m, 5 H), 7.6–7.8 (m, 2 H), 7.8–8.0 (m, 2 H). Anal. Calcd for C₂₁H₂₀O₃: C, 78.72; H, 6.29. Found: C, 78.66; H, 6.32.

General Procedure for the Photochemical Reactions of Epoxy-naphthoquinones 3 with Aldehydes. A solution of **3** (1 g) and aldehyde (10 equiv with respect to **3** in the case of aliphatic aldehydes and 5 equiv with respect to **3** in the case of aromatic ones) in 500 mL of benzene in a Pyrex vessel was bubbled with N₂ for 10 min and then irradiated under cooling with water. The progress of the reaction was followed by GC or HPLC. After **3** had been completely consumed, the irradiation was ceased. In the reactions with aliphatic aldehydes, the solvent and excess aldehydes were removed under reduced pressure, and the resulting oil was chromatographed over a silica gel column with 5% ether/hexane as the eluant. The first component was endo adduct **8**, and the second was exo adduct **9**. In the reactions with aromatic aldehydes, after the solvent was removed under reduced pressure, the resulting mixture was treated with KMnO₄ solution in acetone–water (1:1) overnight at room temperature. Then, the mixture was extracted with chloroform, and the organic layer was washed successively with NaHSO₃ and NaHCO₃ and dried (Na₂SO₄). The products were separated by chromatography on silica gel column with 5% ether/hexane as the eluant. Exo adduct **9** eluted first, followed endo adduct **8**. Yields and physical properties of **8** and **9** are summarized in Tables I, II, and V. Selected ¹³C NMR data are follows: **8a** (CDCl₃) δ 202.2 (C=O), 195.1 (C=O), 134.3 (s), 133.4 (d), 133.2 (d), 131.3 (s), 130.6 (d), 130.2 (d), 106.8 (s), 90.5 (s), 80.8 (d), 20.8 (q), 20.0 (q), 14.5 (q). **9a** (CDCl₃) δ 205.8 (C=O), 198.0 (C=O), 134.1 (s), 133.3 (d), 133.2 (d), 132.4 (s), 129.7 (d), 129.3 (d), 107.3 (s), 89.9 (s), 78.5 (d), 22.3 (q), 17.7 (q), 17.0 (q).

General Procedure for the Photochemical Reaction of 3 with Ketones. Typically, the procedure for the reaction of **3a** with acetone was used. A solution of **3a** (1 g) in 600 mL of acetone was irradiated for 30 min. After removal of the solvent in vacuo, the resulting semisolid material was triturated with hexane, giving colorless crystals of **14a** (1.09 g, 85%).

Detailed reaction conditions, product yields, and physical properties were summarized in Table VI and V: ¹³C NMR (CDCl₃) for **14a** δ 203.3 (C=O), 196.3 (C=O), 134.2 (s), 133.6 (d), 133.2 (d), 131.4 (s), 130.5 (d), 130.3 (d), 106.2 (s), 92.4 (s), 83.9 (s), 25.4 (q), 24.1 (q), 22.2 (q), 19.4 (q).

Photoinduced Oxygenation of 3a in Benzene. A solution of **3a** (500 mg) in 600 mL of benzene was bubbled with O₂ for 30

(20) Kato, H.; Tezuka, H.; Yamaguchi, K.; Nowada, K.; Nakamura, Y. *J. Chem. Soc., Perkin Trans. 1* 1978, 1029.

(21) Hamburger, H.; Huisgen, R. *J. Chem. Soc., Chem. Commun.* 1971, 1190.

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

Table V. Physical Properties of 1,3-Dioxolanes

compd	formula	atom	elemental analysis		IR (KBr) ν_{\max} , cm^{-1}	$^1\text{H NMR}$ (CDCl_3), δ (J , Hz)
			calcd	found		
8e	$\text{C}_{18}\text{H}_{22}\text{O}_4$	C	70.81	70.94	1680, 1600, 1160	0.77 (t, $J = 6$, 3 H), 0.89 (t, $J = 6$, 3 H), 1.2-1.6 (m, 5 H), 7.6-8.2 (m, 4 H)
		H	6.99	6.87		
9e	$\text{C}_{18}\text{H}_{22}\text{O}_4$	C	70.81	70.97	1690, 1595, 1155	0.90 (t, $J = 6$, 3 H), 0.94 (t, $J = 6$, 3 H), 1.2-1.7 (m, 5 H), 7.7-8.2 (m, 4 H)
		H	6.99	7.03		
8f	$\text{C}_{20}\text{H}_{18}\text{O}_4$	C	74.52	74.76	1705, 1680, 1595, 1170	2.62 (dd, $J = 4$, 16, 1 H), 2.96 (dd, $J = 8$, 16, 1 H), 7.2 (m, 5 H), 7.6-7.8 (m, 2 H), 8.0-8.2 (m, 1 H)
		H	5.63	5.68		
9f	$\text{C}_{20}\text{H}_{18}\text{O}_4$	C	74.52	74.36	1690, 1590, 1165	2.9 (m, 1 H), 2.98 (m, 1 H), 7.2 (m, 5 H), 7.6-8.0 (m, 4 H)
		H	5.63	5.90		
8g	$\text{C}_{26}\text{H}_{22}\text{O}_4$	C	78.37	78.40	1700, 1680, 1600, 1180	3.96 (d, $J = 10$, 1 H), 7.0-7.4 (m, 10 H), 7.6-7.8 (m, 2 H), 7.9-8.2 (m, 2 H)
		H	5.57	5.52		
9g	$\text{C}_{26}\text{H}_{22}\text{O}_4$	C	78.37	78.45	1705, 1685, 1595, 1290	4.20 (d, $J = 10$, 1 H), 7.1-7.5 (m, 10 H), 7.6-8.0 (m, 4 H)
		H	5.57	5.62		
8h	$\text{C}_{24}\text{H}_{34}\text{O}_4$	C	74.57	74.27	2950, 1690, 1580, 1160	0.88 (t, $J = 6$, 3 H), 1.0-1.5 (m, 20 H), 7.6-8.1 (m, 4 H)
		H	8.87	9.15		
8j	$\text{C}_{20}\text{H}_{18}\text{O}_5$	C	70.99	70.55	1680, 1600, 1360	3.70 (OCH_3), 6.70 (d, $J = 7$, 2 H), 6.96 (d, $J = 7$, 2 H), 7.9-8.3 (m, 4 H)
		H	5.36	5.52		
9j	$\text{C}_{20}\text{H}_{18}\text{O}_5$	C	70.99	71.03	1685, 1590, 1340	3.76 (OCH_3), 6.86 (d, $J = 7$, 2 H), 7.24 (d, $J = 7$, 2 H), 7.6-8.0 (m, 4 H)
		H	5.36	5.34		
8k	$\text{C}_{20}\text{H}_{18}\text{O}_4$	C	74.52	74.77	1680, 1595, 1350	2.26 (s, 3 H), 6.92 (d, $J = 7$, 2 H), 7.9-8.3 (m, 4 H)
		H	5.63	5.92		
9k	$\text{C}_{20}\text{H}_{18}\text{O}_4$	C	74.52	74.77	1685, 1600, 1370	2.34 (s, 3 H), 7.16 (m, 4 H), 7.6-8.0 (m, 4 H)
		H	5.63	5.66		
8l	$\text{C}_{19}\text{H}_{16}\text{O}_4$	C	74.01	74.33	1680, 1590, 1350	7.2 (m, 5 H), 7.9-8.2 (m, 4 H)
		H	5.23	5.51		
9l	$\text{C}_{19}\text{H}_{16}\text{O}_4$	C	74.01	74.22	1690, 1590, 1350	6.94 (d, $J = 6$, 2 H), 7.16 (d, $J = 6$, 2 H), 7.9-8.2 (m, 4 H)
		H	5.23	5.33		
8m	$\text{C}_{19}\text{H}_{15}\text{ClO}_4$	C	66.58	66.41	1680, 1600, 1350	6.94 (d, $J = 6$, 2 H), 7.16 (d, $J = 6$, 2 H), 7.9-8.2 (m, 4 H)
		H	4.41	4.37		
9m	$\text{C}_{19}\text{H}_{15}\text{ClO}_4$	Cl	10.34	10.22	1685, 1595, 1340	7.26 (d, $J = 6$, 2 H), 7.32 (d, $J = 6$, 2 H), 7.6-8.0 (m, 4 H)
		H	4.41	4.22		
14a	$\text{C}_{15}\text{H}_{16}\text{O}_4$	C	69.21	69.20	2990, 1680, 1590, 1150	1.18 (s, 3 H), 1.40 (s, 3 H), 1.50 (s, 3 H), 1.70 (s, 3 H), 7.6-7.8 (m, 2 H), 8.0-8.2 (m, 2 H)
		H	6.20	6.27		
14b	$\text{C}_{17}\text{H}_{20}\text{O}_4$	C	70.81	70.77	2990, 1685, 1595, 1460, 1275, 1170	0.84 (t, $J = 7$, 3 H), 1.00 (t, $J = 7$, 3 H), 1.53 (s, 3 H), 1.67 (s, 3 H), 1.26 (q, $J = 7$, 2 H), 1.76 (q, $J = 2$ H), 7.5-7.7 (m, 2 H), 7.9-8.0 (m, 2 H)
		H	6.99	6.85		
14c	$\text{C}_{17}\text{H}_{18}\text{O}_4$	C	71.31	71.42	2980, 1690, 1595, 1375, 1275, 1160	1.52 (s, 3 H), 1.68 (s, 3 H), 1.2-1.9 (m, 8 H), 7.6-7.8 (m, 2 H), 7.9-8.2 (m, 2 H)
		H	6.34	6.29		
14d	$\text{C}_{18}\text{H}_{20}\text{O}_4$	C	71.98	72.00	2930, 1680, 1590, 1445, 1375, 1270	1.48 (s, 3 H), 1.69 (s, 3 H), 1.0-2.0 (m, 10 H), 7.6-7.8 (m, 2 H), 8.0-8.2 (m, 2 H)
		H	6.71	6.75		
14e	$\text{C}_{20}\text{H}_{18}\text{O}_4$	C	74.52	74.59	2990, 1680, 1600, 1250	7.2-7.5 (m, 5 H), 7.6-7.7 (m, 2 H), 7.8-8.0 (m, 2 H)
		H	5.63	5.65		
25	$\text{C}_{16}\text{H}_{18}\text{O}_4$	C	70.05	70.02	2990, 1690, 1600, 1150	0.93 (t, $J = 6$, 3 H), 1.03 (t, $J = 7$, 3 H), 1.22 (d, $J = 7$, 3 H), 1.6-2.4 (m, 4 H), 4.08 (q, $J = 7$, 1 H), 7.6-8.1 (m, 4 H)
		H	6.61	6.72		
26	$\text{C}_{16}\text{H}_{18}\text{O}_4$	C	70.05	70.11	2990, 1695, 1600, 1150	0.93 (t, $J = 6$, 3 H), 0.96 (t, $J = 6$, 3 H), 1.30 (d, $J = 7$, 3 H), 1.6-2.4 (m, 4 H), 4.33 (q, $J = 7$, 3 H), 7.7-8.0 (m, 4 H)
		H	6.61	6.62		
28	$\text{C}_{18}\text{H}_{22}\text{O}_4$	C	71.50	71.72	2990, 1695, 1590, 1140	0.92 (s, 9 H), 1.20 (d, $J = 6$, 3 H), 1.73 (s, 3 H), 1.73 and 2.22 (AB q, $J = 14$, 2 H), 4.00 (q, $J = 6$, 1 H), 7.6-8.0 (m, 4 H)
		H	7.33	7.19		
29	$\text{C}_{18}\text{H}_{22}\text{O}_4$	C	71.50	71.52	2990, 1680, 1600, 1150	0.91 (s, 9 H), 1.27 (d, $J = 7$, 3 H), 1.70 (s, 3 H), 1.63 and 2.55 (AB q, $J = 14$, 2 H), 4.20 (q, $J = 7$, 1 H), 7.7-8.0 (m, 4 H)
		H	7.33	7.53		
30	$\text{C}_{18}\text{H}_{22}\text{O}_4$	C	71.50	71.37	2990, 1680, 1595, 1150	0.88 (s, 9 H), 1.18 (d, $J = 7$, 3 H), 1.55 (s, 3 H), 1.73 and 2.77 (AB q, $J = 13$, 2 H), 4.07 (q, $J = 7$, 1 H), 7.6-8.0 (m, 4 H)
		H	7.33	7.54		
31	$\text{C}_{18}\text{H}_{22}\text{O}_4$	C	71.50	71.58	2980, 1695, 1600, 1155	0.86 (s, 9 H), 1.32 (d, $J = 7$, 3 H), 1.47 (s, 3 H), 1.80 and 2.66 (AB q, $J = 12$, 2 H), 4.22 (q, $J = 7$, 1 H), 7.7-8.1 (m, 4 H)
		H	7.33	7.47		
32	$\text{C}_{17}\text{H}_{20}\text{O}_4$	C	70.81	70.66	2990, 1685, 1600, 1450	0.95 (t, $J = 6$, 3 H), 1.10 (t, $J = 6$, 3 H), 1.09 (s, 3 H), 1.38 (s, 3 H), 1.6-2.4 (m, 4 H), 7.6-8.0 (m, 4 H)
		H	6.99	7.05		
33	$\text{C}_{19}\text{H}_{24}\text{O}_4$	C	72.12	71.82	2980, 1685, 1590, 1270, 920, 730	0.89 (s, 9 H), 1.18 (s, 3 H), 1.42 (s, 3 H), 1.75 (s, 3 H), 1.75 and 2.33 (AB q, $J = 14$, 2 H), 7.6-7.7 (m, 2 H), 7.8-7.9 (m, 2 H)
		H	7.65	7.76		
34	$\text{C}_{19}\text{H}_{24}\text{O}_4$	C	72.12	71.22	2990, 1680, 1590, 1270, 1150, 990	0.95 (s, 9 H), 1.23 (s, 3 H), 1.39 (s, 3 H), 1.52 (s, 3 H), 1.73 and 2.75 (AB q, $J = 14$, 2 H), 7.6-7.8 (m, 2 H), 7.8-7.9 (m, 2 H)
		H	7.65	7.74		
35	$\text{C}_{24}\text{H}_{26}\text{O}_4$	C	76.16	76.22	2990, 1700, 1590, 1275, 1150, 925	1.13 (s, 3 H), 1.30 (s, 3 H), 1.33 (s, 3 H), 1.40 (s, 3 H), 1.56 (s, 3 H), 2.13 and 2.80 (AB q, $J = 14$, 2 H), 7.0-7.4 (m, 5 H), 7.5-7.7 (m, 3 H), 8.0-8.1 (m, 1 H)
		H	6.93	7.03		
36	$\text{C}_{24}\text{H}_{26}\text{O}_4$	C	76.16	76.02	2990, 1690, 1600, 1150	1.13 (s, 3 H), 1.20 (s, 3 H), 1.23 (s, 3 H), 1.35 (s, 3 H), 1.36 (s, 3 H), 2.20 and 3.20 (AB q, $J = 14$, 2 H), 7.0-7.5 (m, 5 H), 7.5-8.0 (m, 4 H)
		H	6.93	6.88		

min at room temperature and then irradiated for 30 min under a slow stream of O₂ bubbling. The solvent was removed in vacuo to leave a yellow oil, which was separated on a Florisil column with ether/hexane as the eluant, giving 3-acetyl-3-acetoxypthalide (16; 249 mg, 43%) and 3-acetoxy-3-methylisochroman-1,4-dione (17); 75 mg, 13%).^{2c}

16: mp 97-99 °C; mass spectrum, m/e (relative intensity) 218 (M⁺ - 18, 1), 192 (30), 191 (20), 176 (5), 175 (7), 148 (100). Anal. Calcd for C₁₂H₁₀O₅: C, 61.54; H, 4.30. Found: C, 61.23; H, 4.65.

17: mp 101-102 °C; mass spectrum, m/e (relative intensity) 218 (M⁺ - 18, 3), 191 (25), 148 (100). Anal. Calcd for C₁₂H₁₀O₅: C, 61.54; H, 4.30. Found: C, 61.28; H, 4.71.

To a benzene solution of 3a (500 mg, in 600 mL) was added a solution of Rose Bengal (30 mg) in 10 mL of methanol. The solution was bubbled with O₂ for 30 min and then irradiated for 30 min under a slow stream of O₂ bubbling. Separation of the products on a Florisil column gave 16 (394 mg, 68%) and 17 (93 mg, 16%).

A solution of 3a (500 mg) and β-carotene (30 mg) in 600 mL of benzene was similarly irradiated for 1 h. The starting epoxynaphthoquinone 3a was recovered (260 mg), and the products were the dimers 6a (60 mg, 25%) and 6b (20 mg, 8.3%).

Acknowledgment. I am most grateful to Professor K. Maruyama for first attracting my interest to the photo-

chemistry of epoxynaphthoquinones and for regularly reinforcing that interest and to Professor H. Suzuki for his discussions and valuable comments on the manuscript. This work was supported by the Saneyoshi Scientific Foundation.

Registry No. 3a, 53948-58-6; 3b, 63688-80-2; 3c, 74954-87-3; 3d, 85304-73-0; 3e, 54328-51-7; 6a, 73198-12-6; 6b, 73245-74-6; 7a, 75-07-0; 7b, 123-38-6; 7c, 123-72-8; 7d, 78-84-2; 7e, 97-96-1; 7f, 122-78-1; 7g, 947-91-1; 7h, 112-54-9; 7i, 555-16-8; 7j, 123-11-5; 7k, 104-87-0; 7l, 100-52-7; 7m, 104-88-1; 8a, 69979-43-7; 8b, 69918-94-1; 8c, 69918-95-2; 8d, 69918-96-3; 8e, 85304-74-1; 8f, 85304-75-2; 8g, 85304-76-3; 8h, 85304-77-4; 8i, 69918-97-4; 8j, 73624-01-8; 8k, 73624-02-9; 8l, 73624-03-0; 8m, 73624-04-1; 9a, 69918-98-5; 9b, 69979-39-1; 9c, 69979-40-4; 9d, 69979-41-5; 9e, 85353-58-8; 9f, 85353-59-9; 9g, 85353-60-2; 9i, 69979-42-6; 9j, 73678-76-9; 9k, 73678-77-0; 9l, 73678-78-1; 9m, 73678-79-2; 14a, 69918-99-6; 14b, 69919-00-2; 14c, 69919-01-3; 14d, 69919-02-4; 14e, 82279-21-8; 16, 75761-78-3; 17, 75761-79-4; 25, 85304-78-5; 26, 85353-61-3; 28, 85304-79-6; 29, 85353-62-4; 30, 85304-80-9; 31, 85353-63-5; 32, 85304-81-0; 33, 74954-88-4; 34, 74954-89-5; 35, 85304-82-1; 36, 85304-83-2; 42, 77455-25-5; 43, 85304-84-3; O₂, 7782-44-7; acetone, 67-64-1; 2-pentanone, 107-87-9; cyclopentanone, 120-92-3; cyclohexanone, 108-94-1; acetophenone, 98-86-2.

Photochemical Rearrangements of β,γ-Cyclopropyl-β',γ'-epoxy Ketones

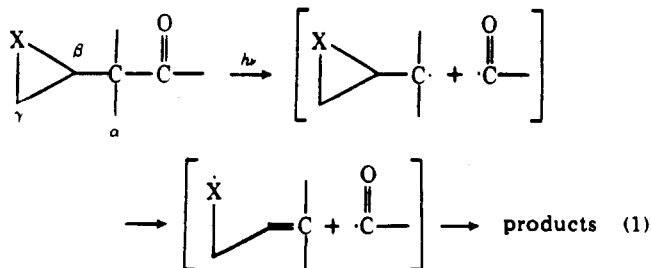
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Received December 3, 1982

Ketones 1-5 have been prepared and photolyzed in benzene and in benzene-methanol (λ > 280 nm). Major volatile products were isolated by gas chromatography and their structures determined by a combination of spectroscopic and chemical methods. The products from 1-4 can be explained by way of α cleavage and selective fission of the carbon-oxygen bond of the epoxide, according to eq 1 (X = O). No effective competition from cleavage of the cyclopropane ring (eq 1, X = CH₂) is observed. Reaction of 2 is slow because of steric crowding, and there is evidence for a small amount of competitive photoisomerization of 2 to 1. In contrast with 1-4, ketone 5 decarbonylates with formation of 5a.

Previous investigations have provided good evidence that a major pathway in the photolysis of β,γ-cyclopropyl ketones is α cleavage, opening of the resultant cyclopropylmethyl radical to homoallyl under stereoelectronic control, and then product formation from the radical pair or biradical, as depicted in eq 1 (X = CH₂).^{1,2} The photo-



tochemistry of β,γ-epoxy ketones follows an analogous path,^{3,4} except that here opening of the oxirane ring occurs

through preferred carbon-oxygen bond cleavage, with no evidence for the influence of stereoelectronic factors;⁵⁻⁷ this is shown in eq 1 (X = O). These conclusions led us to inquire what pathways would be favored in the photochemistry of ketones incorporating both a cyclopropyl and

(3) Carlson, R. G.; Huber, J. H.-A.; Henton, D. E. *J. Chem. Soc., Chem. Commun.* 1973, 223. Murray, R. K., Jr.; Goff, D. L. *Ibid.* 1973, 881. Murray, R. K., Jr.; Morgan, T. K., Jr.; Polley, J. A. S.; Andruskiewicz, C. A., Jr.; Goff, D. L. *J. Am. Chem. Soc.* 1975, 97, 938.

(4) Ayril-Kaloustian, S.; Wolff, S.; Agosta, W. C. *J. Org. Chem.* 1978, 43, 3314.

(5) Ayril-Kaloustian, S.; Agosta, W. C. *J. Am. Chem. Soc.* 1980, 102, 314.

(6) For recent evidence suggesting the absence of stereoelectronic control also in the opening of epoxymethyl radicals generated thermally, see: Barton, D. H. R.; Motherwell, R. S. H.; Motherwell, W. B. *J. Chem. Soc., Perkin Trans. 1* 1981, 2363.

(7) Recently reported observations suggest that stereoelectronic effects are important, however, in directing the photochemistry of two isomeric β,γ-epoxy α-diketones: Liao, C. C.; Lin, H. S.; Hseu, T. H.; Tang, C. P.; Wang, J. L. *J. Am. Chem. Soc.* 1982, 104, 292. One difference between the two classes of compounds is the lower energy of the first excited states of α-diketones ($E_S \approx 65$, $E_T \approx 56$ kcal/mol) in comparison with those of alkanones ($E_S \approx 88$, $E_T \approx 80$ kcal/mol). The manifestation of stereoelectronic effects may well be associated with this lower energy, as well as with the availability in these α-diketones of several competitive pathways for reaction.

(1) Smith, A. B., III; Brodsky, L.; Wolff, S.; Agosta, W. C. *J. Chem. Soc., Chem. Commun.* 1975, 509. Hess, L. D.; Jacobson, J. L.; Schaffner, K.; Pitts, J. N., Jr. *J. Am. Chem. Soc.* 1967, 89, 3684.

(2) Takakis, I. M.; Agosta, W. C. *J. Am. Chem. Soc.* 1979, 101, 2383.