chloride and anisaldehyde by the method of Smith et al.[21] in 67% yield, mp 83-85 °C (lit.[21] mp 84-85.5 °C).

1-(4-Methoxyphenyl)-2-(4-methylphenyl)ethanol (2c). Ethanol **1c**, 6.0 g (22 mmol) in methanol, was methylated with 3.0 g (70 mmol) of freshly distilled diazomethane in ether. After the excess diazomethane was allowed to blow off in a hood, the ether solution was extracted with 2 N NaOH and dried over $MgSO_4$ and the ether removed at 50 °C. The alcohol **2c**, 5.6 g (87%), was obtained as a white amorphous solid from hexane, mp 42-44 °C. IR (KBr): 3328 (OH str), 3004 (Ar C-H str) 1250 (C-O str) cm^{-1}. NMR ($CDCl_3$): 2.29 (s, 3 H), 2.73 (d, J = 3.6 Hz, 1 H), 2.95 (d, J = 8.1 Hz, 2 H), 3.78 (s, 3 H), 4.79 (t of d, 1 H), 6.77-7.30 (m, 8 H) ppm. UV λ (log ϵ_{max}): 223 (4.25), 273 (3.33), 281 (3.23) nm.

Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.44. Found: C, 79.61; H, 7.52.

1,2-Bis(4-methoxyphenyl)ethanol (2d). Alcohol **2d** was prepared by the $NaBH_4$ reduction of desoxyanisoin in 87% yield, mp 112-113 °C (lit.[22] mp 110 °C).

1-(4-Methoxyphenyl)-2-(4-nitrophenyl)ethanol (2e). Ethanol **1e** was methylated with diazomethane using the procedure described above to give alcohol **2e** in 84% yield, mp 113-114 °C (lit.[23] mp 113-115 °C).

(21) Smith, G. G.; Bagley, F. D. *J. Am. Chem. Soc.* **1961**, *83*, 3647.
(22) Buck, J. S.; Jenkins, S. S. *J. Am. Chem. Soc.* **1929**, *51*, 2166.
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1-Methoxy-1-(4-methoxyphenyl)-2-phenylethane (3a). The procedure of Johnstone[24] was used to methylate 1,2-diarylethanol **2a**. Ethanol **2a**, 0.91 g (4.0 mmol), was added to a suspension of 0.90 g (16 mmol) powdered KOH in 0.5 mL (8 mmol) of freshly distilled methyl iodide. After being stirred for 30 min, the mixture was poured into water, extracted with CH_2Cl_2, and then washed with water. Removal of CH_2Cl_2 and recrystallization from aqueous methanol yielded 0.82 g (84%) of pale yellow crystals, mp 46-47 °C. IR (KBr): 3034 (Ar C-H str), 2914 (R C-H str), 1240 (C-O str) cm^{-1}. NMR ($CDCl_3$): 2.9-3.6 (m, 5 H), 3.78 (s, 3 H), 4.27 (t, J = 8.1 Hz, 1 H), 6.8-7.2 (m, 9 H) ppm. UV λ (log ϵ_{max}): 225 (4.15), 274 (3.20), 281 (3.13) nm.

Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.44. Found: C, 79.46; H, 7.38.

Acknowledgment. We gratefully acknowledge funding for this project provided by the U.S. Department of Agriculture—Wood Utilization Research Program.

Registry No. **1a**, 73049-07-7; **1b**, 110995-89-6; **1c**, 110995-90-9; **1d**, 110995-91-0; **1e**, 110995-92-1; **2a**, 5422-47-9; **2b**, 6279-23-8; **2c**, 113160-00-2; **2d**, 20498-71-9; **2e**, 20498-72-0; **3a**, 113160-01-3; *p*-anisaldehyde, 123-11-5; benzylmagnesium bromide, 1589-82-8; (*p*-chlorobenzyl)magnesium chloride, 874-72-6; desoxyanisoin, 120-44-5.

(24) Johnstone, R. W.; Rose, M. E. *Tetrahedron* **1979**, *35*, 2169.

Photoinduced Reductive Addition Reactions of 2-Alkenoyl-1,4-benzoquinones with Alcohols

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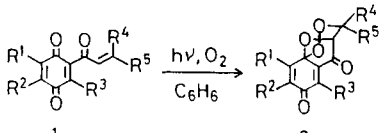
Received October 7, 1986

Irradiation of 2-alkenoyl-3,5-dimethyl-1,4-benzoquinones **1** in alcohol under a nitrogen atmosphere afforded two isomeric adducts: benzofuranone derivatives **4** and alkenyl ether derivatives **5**. The ratios of **4** to **5** depended both on the nature of the alkenoyl substituents and on the alcohols used as solvent. Irradiation of some quinones **1** dissolved in *tert*-butyl alcohol gave, however, 3-substituted chromone derivatives **13** as additional products.

Photochemical reactions of isoprenoid 1,4-quinones, e.g., plastoquinone,[1] ubiquinone (coenzyme Q)[2], and vitamin K analogues (menaquinone and phylloquinone)[3] have been extensively investigated under several conditions because these quinones are known to play an important role in biological processes such as electron transport and oxidative phosphorylation.[4] From the anaerobic photosynthetic bacterium, *Chlorobium thiosulphatophilum*, for example, chlorobiumquinone (1′-oxomenaquinone 7), which is an alkenoyl-1,4-quinone with an olefinic double bond and a carbonyl group in the side chain, was isolated.[5] Irradiations of isoprenoid 1,4-quinones under aerobic conditions give trioxane, hydroperoxide, and aldehyde, but under anaerobic conditions intramolecular cyclization products such as chromene are produced.[1-3] Investigation of the photochemical reactions of alkenoyl quinones **1** is therefore of interest from both the biological and the photochemical point of view.

Recently, it has been reported[6] that irradiation of alkenoyl quinones **1** in benzene under aerobic conditions affords the relatively stable cyclic peroxides **2** (eq 1). In



1 2 (1)

a preliminary paper we reported[7] that irradiation of 2-alkenoyl-3,5-dimethyl-1,4-benzoquinones in methanol or ethanol under anaerobic conditions gave two isomeric

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(2) Moore, H. W.; Folkers, K. *Justus Liebigs Ann. Chem.* **1965**, *684*, 212. Morimoto, H.; Imada, I.; Goto, G. *Ibid.* **1970**, *735*, 65.
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(4) Brodie, A. F. In *Biochemistry of Quinones*; Morton, R. A., Ed.; Academic: London, 1965; p 384.
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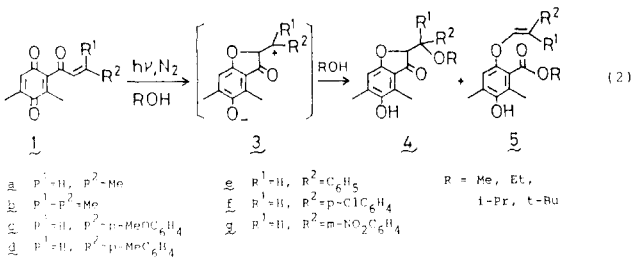
0022-3263/88/1953-1507$01.50/0

Table I. Photochemical Reaction of 1a–g with Alcohol

compd	substituent R^1	substituent R^2	yield and ratio of products, %[a] in MeOH 4M + 5M (4M/5M)	in EtOH 4E + 5E (4E/5E)	in *i*-PrOH 4P + 5P (4P/5P)	in *t*-BuOH[b] 4B + 5B (4B/5B)
1a	H	Me	97 (13/87)	96 (9/91)	87 (9/91)[c]	56 (12/88)[c]
1b	Me	Me	96 (91/9)	94 (78/22)	95 (61/39)	93 (55/45)
1c	H	*p*-$MeOC_6H_4$	97 (100/0)	93 (100/0)	92 (100/0)	62 (100/0)[d]
1d	H	*p*-MeC_6H_4	100 (99/1)	98 (99/1)	98 (92/8)	78 (62/38)[d]
1e	H	Ph	99 (83/17)	98 (77/23)	94 (52/48)	71 (15/85)[e]
1f	H	*p*-ClC_6H_4	98 (79/21)	98 (67/33)	96 (44/56)	50 (8/92)[e]
1g	H	*m*-$NO_2C_6H_4$	92 (20/80)	93 (10/90)	32 (5/95)[f]	8 (0/100)

[a] Isolated yields based on the quinone used. [b] **1a**, **1c**, **1d**, **1e**, **1f**, and **1g** were recovered in 2%, 10%, 13%, 35%, and 88% yields, respectively. [c] Product **13a** was also obtained in 6% and 32% yields, respectively. [d] Products **10** were also obtained in 27% and 6% yields, respectively. [e] Products **13** were also obtained in 5% and 3% yields, respectively. [f] **1g** was recovered in a yield of 63%.

adducts, benzofuranone derivatives **4** and alkenyl ether derivatives **5** (eq 2). This paper will deal with the con-

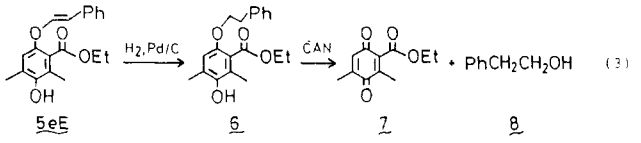


(2)

trolling factors of the reactions, the reaction products and detailed reaction mechanisms.

Results and Discussion

Photochemical Reaction of 2-Alkenoyl-3,5-dimethyl-1,4-benzoquinones 1a–g. Typically, irradiation of an ethanol solution of 2-cinnamoyl-3,5-dimethyl-1,4-benzoquinone (**1e**, 0.01 M) with a light of wavelength longer than 410 nm under a nitrogen atmosphere for 3 h afforded 2-(α-ethoxybenzyl)-5-hydroxy-4,6-dimethylbenzofuran-3(2*H*)-one (**4eE**, 75%) and ethyl 3-hydroxy-2,4-dimethyl-6-styryloxybenzoate (**5eE**, 23%). The structures of **4eE** and **5eE** were determined by their spectral data and the following chemical transformations. The product **4eE** was reduced with sodium borohydride to give the expected reduction product.[7] Another product **5eE** was reduced by catalytic hydrogenation to give **6**.[7] The structure of **5eE** was further supported by the following chemical reactions. Reduction product **6** was oxidized by ammonium cerium(IV) nitrate (CAN) to give 2-(ethoxycarbonyl)-3,5-dimethyl-1,4-benzoquinone (**7**, 96%) and 2-phenylethanol (**8**, 81%) (eq 3, see Experimental Section).



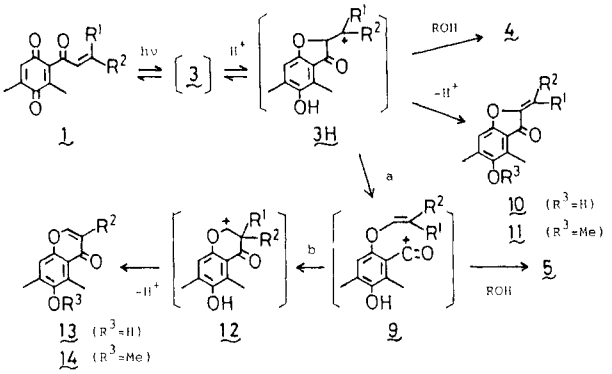
(3)

Similarly, **1e** and other alkenoyl quinones **1a–g** reacted to give two isomeric adducts **4** and **5** in methanol, ethanol, isopropyl alcohol, and *tert*-butyl alcohol. The isomer distributions are summarized in Table I.

As a result of substituent effects on the alkenoyl side chain, reaction of **1a** in alcohols gave predominantly adduct **5a**, while reaction of **1b** gave **4b** as the major product as shown in Table I. This may be due to the fact that reaction intermediate **3b** ($R^1 = R^2 = Me$), with a tertiary carbonium ion, is more stable than **3a** ($R^1 = H$, $R^2 = Me$), with a secondary carbonium ion.

In reactions of **1c–g**, which are para- or meta-substituted cinnamoyl-1,4-benzoquinones, **1c** and **1d**, with electron-donating groups, gave **4c** and **4d**, respectively, as predominant adducts, whereas in the reactions of **1e** and **1f**, the ratio **4f**/**5f** was slightly smaller than that of **4e**/**5e**. In addition, in the reacton of **1g**, which has a much stronger electron-withdrawing nitro group, the ratio **4g**/**5g** was changed dramatically to give **5g** as the predominant product. The ratio **4**/**5** gradually decreases as the decreasing electron-donating character of substituents increases. Hence, it is concluded that intermediate **3** stabilized by an electron-donating group gives predominantly **4**, while intermediate **3** destabilized by an electron-withdrawing group affords a larger amount of **5**.

Scheme I



On the basis of the above experimental results, a possible reaction mechanism in alcohol solution is proposed as follows. The photoexcited **1** cyclizes intramolecularly to form zwitterionic intermediate **3**,[1] which is protonated by the alcohol proton to give cationic intermediate **3H**. When intermediate **3H** is sufficiently stable, alcohol may add to **3H** to give adduct **4**. By contrast, when intermediate **3H** is relatively unstable, cleavage of the C–C bond adjacent to the carbonyl group of **3H** may occur before addition of alcohol to give intermediate **9** (path a) which subsequently results in the formation of **5** as shown in Scheme I.

The isomer distributions were also affected by the character of alcohol solvent. The ratio **4**/**5** decreased on changing from methanol to *tert*-butyl alcohol except with **1a** and **1c**. For example, in reaction of **1b** with MeOH, EtOH, *i*-PrOH, and *t*-BuOH, the ratio **4b**/**5b** decreased as follows: 91:9, 78:22, 61:39, and 55:45. Moreover, in the reactions of **1e** and **1f** with *tert*-butyl alcohol, the ratios **4eB**/**5eB** and **4fB**/**5fB** were less than one, i.e., **5eB** and **5fB** were the major products (see Table I). In addition, in reaction in *tert*-butyl alcohol, **1a** gave another isomerization product, **13**.

These isomer distributions could be rationalized in terms of the following factors. One of the most important controlling factors is accessibility of an alcohol to **3H**. Access of alcohol to **3H** becomes more difficult in the progression

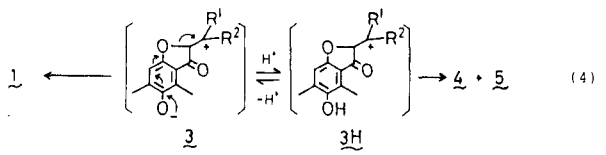
Table II. Photochemical Reaction of 1e in Several Solvents

run	solvent	additive (v/v %)	reactn time, h	yield of product,[a] % 4	5	(4/5)	recovd 1e, %[b]
1	C_6H_6		3	c	c	c	99
2	MeCOMe		3	c	c	c	99
3	MeCN		3	c	c	c	99
4	C_6H_6	AcOH(4)	1	35	38	(48/52)	8[d]
5	C_6H_6	MeOH(6)	1	trace	48	(1/99)	51

[a] The ratios 4/5 were determined by NMR. [b] Isolated yield. [c] Not detected. [d] Product 10e was also obtained in a yield of 17%.

from methanol to *tert*-butyl alcohol because of steric factors. Therefore, formation of 4 decreases in this order and that of 5 via 9 increases. The other factor is the polarity of the alcohols. Stability of intermediate **3H** decreases with decreasing polarity of solvents from methanol to *tert*-butyl alcohol, thus decreasing the ratio **4/5**. The experimental results support this as shown in Figure 1. The ratio **4eE/5eE** decreases with decreasing proportion of ethanol in reacting solvent ($EtOH/C_6H_6$). In other words, the ratio **4eE/5eE** increases with increasing polarity of solvent. Another controlling factor is the acidity of the solvent as reactant. Increasing acidity of solvent favors protonation of **3**, thus facilitating the attack of solvent as a reactant on intermediate **3H**. In practice, in the reaction of **1e** in benzene solution containing acetic acid or methanol, the ratio **4eA/5eA** of the adducts with acetic acid was 48:52, but the ratio **4eM/5eM** of that with methanol was 1:99. Moreover, the total yield of adducts in the reaction with acetic acid was higher than that with methanol (runs 4 and 5 in Table II).

In addition, protonation of **3** to **3H** was supported by the following experimental results. Upon irradiation in a benzene, acetone, and acetonitrile solution, starting material quinone **1e** was mostly recovered (runs 1–3 in Table II). Irradiation of **1e** in benzene solution containing small amount of acetic acid or methanol, however, gave the corresponding adducts (runs 4 and 5 in Table II). Thus, addition of a protic solvent stimulates by protonation of **3** to **3H** the forward reaction,[8] preventing backreacton of **3** to the starting quinone (eq 4). On the other



hand, irradiation of 2-(*p*-methoxycinnamoyl)-3,5-dimethyl-1,4-benzoquinone (**1c**) in *tert*-butyl alcohol gave 2-anisylidene-5-hydroxy-4,6-dimethylbenzofuran-3(2*H*)-one (**10c**, 27%). A similar product **10d** (6%) was also obtained in the reaction of **1d** in *tert*-butyl alcohol. Product **10** could result from deprotonaton from **3H**. This provides support for the postulate that intermediate **3H** is involved.

Irradiation of 2-crotonoyl-3,5-dimethyl-1,4-benzoquinone (**1a**) in *tert*-butyl alcohol afforded an isomerization product, 6-hydroxy-3,5,7-trimethylchromone (**13a**, 32%), together with two isomeric adducts. Analogous isomerization products **13e** and **13f** were obtained, though in low yield, in reactions of **1e** and **1f** in *tert*-butyl alcohol. Product **13** might be formed by cyclization of intermediate **9** via **12** (paths a and b), because of the relatively high electron density of the vinyloxyl group of **9** and the steric con-

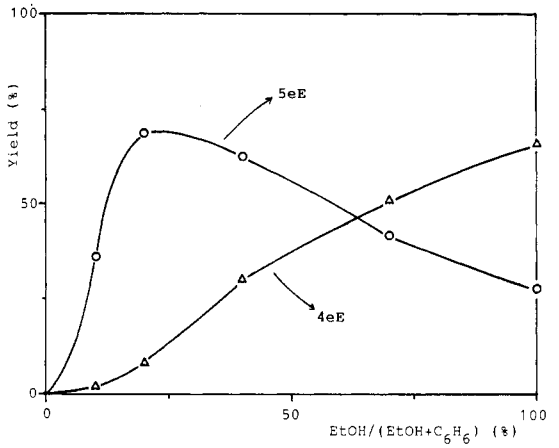
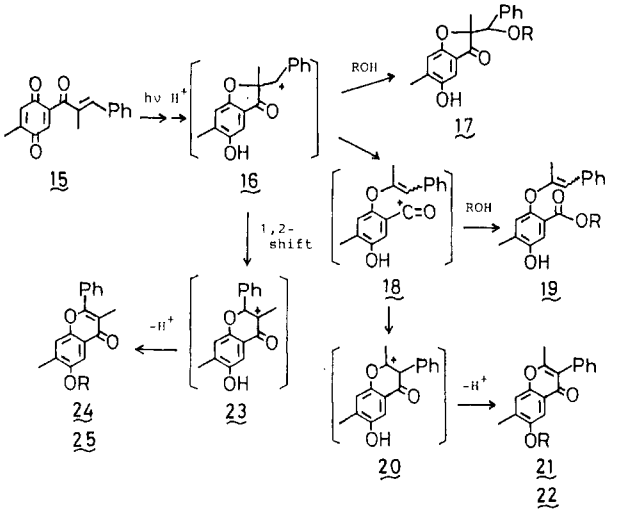


Figure 1. Yields of **4eE** and **5eE** in an ethanol–benzene mixture after irradiation of **1e** for 1 h.

Scheme II



straints impeding addition of bulky alcohol to **9**. Though the yield of product **13e** was very low when a methyl group is present at the 2-position of intermediate **3He** (R^1 = H, R^2 = Ph) addition of alcohol to the corresponding intermediate **16** (see Scheme II) might become more difficult than addition of alcohol to **3He** because of steric hindrance. The electron density of the α-methylvinyloxyl group of **18** resulting from **16** may be higher than that of the vinyloxyl group of **9e**. Intermediate **20** could be more stabilized by the 2-methyl group than intermediate **12e**. Therefore, formation of **20** to give **21** will be more favorable than that of **12e** to give **13e**. In fact, irradiation of 5-methyl-2-(α-methylcinnamoyl)-1,4-benzoquinone (**15**) in *tert*-butyl alcohol gave the corresponding isomerization product **21** (44%) together with its regioisomer **24** (24%).[9] The reaction of **15** gave the isomerization product **21** (6%) even

(8) The reacton of **15** in acetone was examined. The irradiation of **15** in acetone gave only 2-phenylchromone derivative **24** (16%). But the reaction of **15** in acetone containing small amount of water (2%) gave considerable amounts of **24** (29%) and **21** (3%) together with the other adducts. Thus, the addition of a protic solvent to the reaction solution promoted the reaction and gave larger amounts of the products.

(9) Maruyama, K.; Iwamoto, H.; Soga, O.; Takuwa, A.; Osuka, A. *Chem. Lett.* **1985**, 595.

Table III. Yields and Physical Properties of 1

product	yield, %	mp, °C	elemental analysis formula	atom	calcd	found	IR (KBr), cm^{-1}	^{1}H NMR ($CDCl_3$), δ (J, Hz)
1a	60	65–67	$C_{12}H_{12}O_3$	C	70.57	70.64	1650, 1320	1.90 (s, 3 H), 1.92 (d, J = 7, 3 H), 2.05 (s, 3 H), 6.25 (d, J = 16, 1 H), 6.55 (s, 1 H), 6.5–6.9 (m, 1 H)
				H	5.92	5.98		
1b	80	85–87	$C_{13}H_{14}O_3$	C	71.54	71.42	1650, 1310	1.98 (s, 6 H), 2.07 (s, 3 H), 2.25 (s, 3 H), 6.10 (s, 1 H), 6.54 (s, 1 H)
				H	6.47	6.57		
1c	35	110–112	$C_{18}H_{16}O_4$	C	72.96	73.11	1645, 1595	1.98 (s, 3 H), 2.09 (s, 3 H), 3.79 (s, 3 H), 6.54 (s, 1 H),
				H	5.44	5.49	1240	1.98 (s, 3 H), 2.09 (s, 3 H), 3.79 (s, 3 H), 6.54 (s, 1 H), 6.66 (d, J = 16, 1 H), 6.82 (d, J = 8, 2 H), 7.25 (d, J = 16, H), 7.40 (d, J = 8, 2 H)
1d	67	133–135	$C_{18}H_{16}O_3$	C	77.12	77.27	1640, 1315	2.00 (s, 3 H), 2.12 (s, 3 H), 2.38 (s, 3 H), 6.61 (s, 1 H), 6.82 (d, J = 16, 1 H), 7.21 (d, J = 8, 2 H), 7.38 (d, J = 16, 1 H), 7.45 (d, J = 8, 2 H)
				H	5.75	5.90		
1e	85	139–141	$C_{17}H_{14}O_3$	C	76.67	76.89	1640, 1310	2.02 (s, 3 H), 2.13 (s, 3 H), 6.64 (s, 1 H), 6.88 (d, J = 16, 1 H), 7.25–7.65 (m, 6 H)
				H	5.30	5.52		
1f	51	136–138	$C_{17}H_{13}O_3Cl$	C	67.89	68.00	1650, 1320	2.01 (s, 3 H), 2.13 (s, 3 H), 6.61 (s, 1 H), 6.82 (d, J = 16, 1 H), 7.25–7.6 (m, 5 H)
				H	4.36	4.40		
1g	61	139–141	$C_{17}H_{13}O_5N$	C	65.59	65.48	1670, 1650	1.98 (s, 3 H), 2.09 (s, 3 H), 6.57 (s, 1 H), 6.89 (d, J = 16, 1 H), 7.42 (d, J = 16, 1 H), 7.53 (t, J = 8, 1 H), 7.83 (d, J = 8, 1 H), 8.19 (d, J = 8, 1 H), 8.30 (s, 1 H)
				H	4.21	4.27	1630, 1530, 1365	

in methanol. Formation of regioisomer **24** could be explained by 1,2-shift of phenoxyl group in the intermediate **16** via **23**.

Since intermediate **12** could be stabilized by conjugation with lone pair electrons on oxygen adjacent to the cation center, the intermediate **12** might be formed by a 1,2-shift of the carbonyl group of **3H**. However, irradiation of **15** in pure acetone gave only **24** (16%), whereas in the reaction in aqueous acetone (9% water) **15** gave both the isomerization products **21** (18%) and **24** (28%) together with adducts **17H** (R = H, 19%) and **19H** (R = H, 13%). These experimental results suggest that formation of **18** as well as **19** may be assisted by a protic solvent resulting in the formation of product **21**. The other isomer **24** could be derived directly by 1,2-shift of phenoxyl anion from **16** via **23**.

Experimental Section

Melting points were measured on a Yanaco micro-melting point apparatus and uncorrected. Elemental analyses were carried out at the Analytical Center of Kyoto University or by using Yanaco MT-2 CHN Corder. IR spectra were recorded on a Hitachi 260-50 infrared spectrometer. ^{1}H NMR spectra were recorded on a JEOL MH-100 spectrometer using tetramethylsilane as an internal standard. Mass spectra were recorded on a JEOL JMS-DX300 or Hitachi M-80B mass spectrometer. Column chromatography was performed on deactivated silica gel (Wakogel C-200), and TLC was done on Merck silica gel PF_{254} (Type 60) unless otherwise specified.

2-Alkenoyl-1,4-benzoquinones **1** were prepared by the method of Peyton[10] from 2-alkenoyl-3,5-dimethylhydroquinone dimethyl ether. The some dimethyl ethers were synthesized by Friedel–Crafts reaction from 1,4-dimethoxy-2,6-dimethylbenzene and the corresponding alkenoyl chloride. The other dimethyl ethers were synthesized by the aldol condensations from substituted benzaldehyde and 2-acetyl-3,5-dimethylhydroquinone dimethyl ether. The resulting quinone **1** were all recrystallized from benzene–hexane mixture as yellow needles. Yeilds and physical properties of **1** are summarized in Table III.

5-Methyl-2-(α-methylcinnamoyl)-1,4-benzoquinone (**15**) was prepared by the same manner for **1** from 5-methyl-2-(α-methylcinnamoyl)hydroquinone dimethyl ether, which was synthesized by aldol condensation from benzaldehyde and 5-methyl-2-propionylhydroquinone dimethyl ether.

15: 77%; yellow needles, mp 151–152 °C; IR ($CHCl_3$) 1670 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.07 (d, J = 1.5 Hz, 3 H), 2.13 (s, 3 H), 6.57 (m, 1 H), 6.61 (s, 1 H), 7.16 (s, 1 H), 7.30 (s, 5 H). Anal. Calcd for $C_{18}H_{16}O_3$: C, 76.67; H, 5.30. Found: C, 76.80; H, 5.26.

General Procedure for the Photochemical Reaction of 2-Alkenoyl-1,4-benzoquinones 1a–g in Alcohol. A solution of **1** (0.3 mmol) in 30 mL of alcohol was degassed under reduced pressure (aspirator) and bubbled with N_2 for 5 min and then irradiated with a 300-W halogen lamp through a yellow glass filter (Toshiba L-42; <410-nm cutoff) at room temperature for 3 h. After reaction, the solvent was removed under reduced pressure, and the resulting oil was chromatographed on column with benzene as eluent. The first yellow component was the starting quinone **1**, the second was **5**, all of which had been *trans*-alkenyloxy groups together with a trace of cis one, and the third was **4**, which showed a characteristic light bluish fluorescence when exposed to ultraviolet light on TLC. The all of the adducts **4** were consisted of the diastereoisomers, but a major product comprised over 90% of the diastereoisomers. The NMR spectral data of **4** should be shown for the major isomer to prevent complications unless otherwise noted. Yields of **4** and **5** are summarized in Table I. The physical properties of **4** and **5** are tabulated in Table IV.

Photochemical Reaction of 1a. The adducts 2-(1-alkoxyethyl)-5-hydroxy-4,6-dimethylbenzofuran-3(2*H*)-ones **4a** were all pale yellow oils and alkyl 3-hydroxy-2,4-dimethyl-6-(1-propenyloxy)benzoates **5a** were all colorless oils.

In the reaction of **1a** in isopropyl and *tert*-butyl alcohols, the fourth component of the column fraction gave 6-hydroxy-3,5,7-trimethylchromone (**13a**) in 6% and 32% yields, respectively. **13a**: colorless solid, mp 167–170 °C; IR (CCl_4) 3600, 3400, 1640, 1615, 1460 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.94 (s, 3 H), 2.32 (s, 3 H), 2.79 (s, 3 H), 5.15 (br s, 1 H), 7.04 (s, 1 H), 7.64 (s, 1 H).

The trimethylchromone **13a** was methylated by methyl iodide and potassium carbonate in dry acetone at 50–60 °C for 1.5 h. The reacton mixture was filtered and the solvent was evaporated in vacuo. After purification by TLC (C_6H_6), 6-methoxy-3,5,7-trimethylchromone (**14a**) was obtained as colorless oil: 80%; IR (CCl_4) 1655, 1610, 1470, 1165 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.84 (s, 3 H), 2.28 (s, 3 H), 2.63 (s, 3 H), 3.59 (s, 3 H), 6.86 (s, 1 H), 7.45 (s, 1 H); MS, for $C_{13}H_{14}O_3$ *m/e* 218.0923 (theory 218.0942). These data of **14a** agreed with that of the authentic sample.[11]

Photochemical Reaction of 1b. The adducts 2-(1-alkoxy-1-methylethyl)-5-hydroxy-4,6-dimethylbenzofuran-3(2*H*)-ones **4b** were all pale yellow prisms and alkyl 3-hydroxy-2,4-dimethyl-6-(2-methyl-1-propenyloxy)benzoates **5b** were all colorless oils.

Photochemical Reaction of 1c. The reacton of **1c** with alcohols gave adducts **4c** but not **5c**. The adducts 2-(α-alkoxyanisyl)-5-hydroxy-4,6-dimethylbenzofuran-3(2*H*)-ones **4c** were all yellow solids.

In the reacton with *tert*-butyl alcohol, the third component of column fraction gave 2-*p*-anisylidene-5-hydroxy-4,6-dimethylbenzofuran-3(2*H*)-one (**10c**, 27%): yellow prisms (benzene–

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hexane), mp 204–206 °C; IR ($CHCl_3$) 3600, 1602, 1255 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.30 (s, 3 H), 2.51 (s, 3 H), 3.76 (s, 3 H), 4.81 (br s, 1 H), 6.60 (s, 1 H), 6.69 (s, 1 H), 6.73 (d, J = 8 Hz, 2 H), 7.69 (d, J = 8 Hz, 2 H).

The obtained product **10c** was methylated by methyl iodide and potassium carbonate in acetone. After TLC ($CHCl_3$) 2-*p*-anisylidene-5-methoxy-4,6-dimethylbenzofuran-3(2*H*)-one (**11c**) was obtained as yellow needles (benzene–hexane) in a 70% yield. **11c**: mp 158–159 °C; IR (CCl_4) 1705, 1650, 1605, 1250 cm^{-1}; ^1H NMR (CCl_4) δ 2.37 (s, 3 H), 2.59 (s, 3 H), 3.70 (s, 3 H), 3.83 (s, 3 H), 6.73 (s, 1 H), 6.93 (s, 1 H), 6.95 (d, J = 8 Hz, 2 H), 7.85 (d, J = 8 Hz, 2 H). These data of **11c** were in agreement with that of the authentic sample.[12]

Photochemical Reaction of 1d. The adducts 2-(α-alkoxy-*p*-methylbenzyl)-5-hydroxy-4,6-dimethylbenzofuran-3(2*H*)-ones **4d** were all pale yellow solids, of which **4dM** showed a high ratio (4:6) of diastereoisomers, and alkyl 3-hydroxy-2,4-dimethyl-6-[(p-methylstyryl)oxy]benzoates **5d** were all pale yellow oils.

In the reaction with *tert*-butyl alcohol, the third yellow component of the column fraction gave 5-hydroxy-4,6-dimethyl-2-*p*-tosylidenebenzofuran-3(2*H*)-one (**10d**, 6%), which was isolated as methyl ether **11d**: yellow needles, mp 122–123 °C; IR (CCl_4) 1700, 1645, 1600, 1240, 1050 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.40 (s, 6 H), 2.62 (s, 3 H), 3.72 (s, 3 H), 6.76 (s, 1 H), 6.95 (s, 1 H), 7.25 (d, J = 8 Hz, 2 H), 7.78 (d, J = 8 Hz, 2 H). Anal. Calcd for $C_{19}H_{18}O_3$: C, 77.53; H, 6.16. Found: C, 77.66; H, 6.28.

Photochemical Reaction of 1e. The adducts 2-(α-alkoxybenzyl)-5-hydroxy-4,6-dimethylbenzofuran-3(2*H*)-ones **4e** were all pale yellow solids, and alkyl 3-hydroxy-2,4-dimethyl-6-(styryloxy)benzoates **5e** were colorless prisms.

In the reacton with *tert*-butyl alcohol, the third component of column fractoin gave 6-hydroxy-5,7-dimethyl-3-phenylchromone (**13e**): 5%; ^1H NMR ($CDCl_3$) δ 2.35 (s, 3 H), 2.81 (s, 3 H), 4.94 (br s, 1 H), 7.12 (s, 1 H), 7.2–7.6 (m, 5 H), 7.85 (s, 1 H). **13e** was methylated to **14e**: colorless solid; IR (CCl_4) 1650, 1245 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.40 (s, 3 H), 2.80 (s, 3 H), 3.70 (s, 3 H), 7.12 (s, 1 H), 7.3–7.6 (m, 5 H), 7.85 (s, 1 H); MS, for $C_{18}H_{16}O_3$ m/e 280.1085 (theory 280.1098).

Photochemical Reaction of 1f. The adducts 2-(α-alkoxy-*p*-chlorobenzyl)-5-hydroxy-4,6-dimethylbenzofuran-3(2*H*)-ones **4f** were all pale yellow microcrystals, and alkyl 2-[(*p*-chlorostyryl)oxy]-3-hydroxy-2,4-dimethylbenzoates **5f** were colorless prisms.

In the reaction with *tert*-butyl alcohol, the third component of column fraction gave 3-(*p*-chlorophenyl)-6-hydroxy-5,7-dimethylchromone (**13f**, 3%), which was methylated to **14f**: colorless solid; IR (CCl_4) 1650 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.39 (s, 3 H), 2.79 (s, 3 H), 3.70 (s, 3 H), 7.13 (s, 1 H), 7.42 (s, 4 H), 7.88 (s, 1 H); MS, for $C_{18}H_{15}O_3Cl$ m/e 314.0744 (theory 314.0709).

Photochemical Reaction of 1g. The data of **4gP** could not been obtained for the low yield. But the existence of **4gP** could be confirmed by the bluish fluorescence on TLC under UV light. The ratio of one was determined by NMR spectrum with the characteristic doublet signal at δ 0.94 and 0.97. The products alkyl 3-hydroxy-2,4-dimethyl-6-[(*m*-nitrostyryl)oxy]benzoates **5g** were all yellow oils.

Reduction of 4eE. To the solution of **4eE** (0.15 mmol) in ethanol (10 mL) was added sodium borohydride (ca. 50 mg) portionwise at about 5 °C. After being stirred at room temperature for overnight, the reaction mixture was worked up in the usual way. The resulting crude product was separated by TLC ($CHCl_3$). The band at R_f 0.5 contained the reducton product 2-(α-ethoxybenzyl)-5-hydroxy-4,6-dimethylbenzofuran: 46%; IR (CCl_4) 3625, 3400, 1460, 1165 cm^{-1}; ^1H NMR (CCl_4) δ 1.23 (t, J = 7 Hz, 3 H), 2.14 and 2.19 (each s, 6 H), 3.52 (q, J = 7 Hz, 2 H), 4.36 (br s, 1 H), 5.29 (s, 1 H), 6.18 (s, 1 H), 6.84 (s, 1 H), 7.15–7.45 (m, 5 H).

The obtained hydroxy benzofuran was acetylated by acetic anhydride and pyridine for overnight at room temperature. The acetate was purified by TLC ($CHCl_3$–C_6H_6, 1:1) and was obtained as colorless oil. 5-Acetoxy-2-(α-ethoxybenzyl)-4,6-dimethylbenzofuran: 93%; IR (CCl_4) 1765, 1215 cm^{-1}; ^1H NMR (CCl_4) δ 1.22 (t, J = 7 Hz, 3 H), 2.12, 2.15, and 2.20 (each s, 9 H), 3.52 (q, J = 7 Hz, 2 H), 5.30 (s, 1 H), 6.33 (s, 1 H), 7.01 (s, 1 H), 7.15–7.45 (m, 5 H). Anal. Calcd for $C_{21}H_{22}O_4$: C, 74.53; H, 6.55. Found: C, 74.34; H, 6.68.

Reduction of 5eE. (i) The adduct **5eE** (0.2 mmol) was methylated by methyl iodide and potassium carbonate in dry acetone. The resulting methylated product was reduced with lithium aluminum hydride (ca. 100 mg) in THF (10 mL) at 40 °C for 30 min. After worked up by usual manner, the crude product was purified by TLC ($CHCl_3$–C_6H_6, 1:1). The band at R_f 0.15 contained the reduction product 3-methoxy-2,4-dimethyl-6-(styryloxy)benzyl alcohol: 67%; IR (CCl_4) 3625, 3480, 1655, 1230 cm^{-1}; ^1H NMR (CCl_4) δ 1.40 (br s, 1 H), 2.20 and 2.27 (each s, 6 H), 3.59 (s, 3 H), 4.54 (s, 2 H), 6.08 (d, J = 13 Hz, 1 H), 6.60 (s, 1 H), 6.99 (d, J = 13 Hz, 1 H), 7.13 (s, 5 H).

The resulting benzyl alcohol was acetylated by acetic anhydride and pyridine at 40 °C for 3 h. The crude product was purified by TLC (C_6H_6). From the band at R_f 0.45, the acetate was obtained as a colorless oil. 3-Methoxy-2,4-dimethyl-6-(styryloxy)benzyl acetate: 80%; IR (CCl_4) 1740, 1655, 1235 cm^{-1}; ^1H NMR (CCl_4) δ 1.91 (s, 3 H), 2.22 (s, 6 H), 3.61 (s, 3 H), 5.05 (s, 2 H), 6.10 (d, J = 13 Hz, 1 H), 6.65 (s, 1 H), 6.97 (d, J = 13 Hz, 1 H), 7.14 (s, 5 H). Anal. Calcd for $C_{20}H_{22}O_4$: C, 73.60; H, 6.79. Found: C, 73.51; H, 6.78.

(ii) A mixture of **5eE** (0.3 mmol) and 10% Pd/C (ca. 100 mg) in ethanol–ethyl acetate (10 mL, 1:1) was stirred under hydrogen atmosphere at room temperature for overnight. After removal of catalyst, the solvent was evaporated in vacuo, and the residue was chromatographed on TLC ($CHCl_3$). The band at R_f 0.25 contained reduction product **6**. Ethyl 3-hydroxy-2,4-dimethyl-6-phenethylbenzoate (**6**): 80%; IR (CCl_4) 3625, 3450, 1735 cm^{-1}; ^1H NMR (CCl_4) δ 1.25 (t, J = 7 Hz, 3 H), 1.94 (s, 3 H), 2.02 (s, 3 H), 2.69 (t, J = 7 Hz, 2 H), 3.94 (t, J = 7 Hz, 2 H), 4.16 (q, J = 7 Hz, 2 H), 4.95 (br s, 1 H), 6.18 (s, 1 H), 7.09 (s, 5 H).

The ethyl hydroxybenzoate **6** was acetylated by acetic anhydride and pyridine. The product was purified by TLC ($CHCl_3$). From the band at R_f 0.4, the acetate was given as a colorless oil. Ethyl 3-acetoxy-2,4-dimethyl-6-phenethylbenzoate: 98%; IR (CCl_4) 1765, 1735, 1265, 1205 cm^{-1}; ^1H NMR (CCl_4) δ 1.26 (t, J = 7 Hz, 3 H), 1.95 and 2.00 (each s, 6 H), 2.16 (s, 3 H), 2.95 (t, J = 7 Hz, 2 H), 4.03 (t, J = 7 Hz, 2 H), 4.17 (q, J = 7 Hz, 2 H), 6.44 (s, 1 H), 7.12 (s, 5 H). Anal. Calcd for $C_{21}H_{24}O_5$: C, 70.76; H, 6.79. Found: C, 70.91; H, 6.81.

Oxidation of 6. The ethyl phenethylbenzoate **6** (0.15 mmol), which was obtained by the catalytic hydrogenation of **5eE** as described above, was oxidized by ammonium cerium(IV) nitrate (CAN, 200 mg) in acetonitrile–water (for 5 min in ice–water bath).[10] After worked up by the usual way, the products were isolated by TLC (C_6H_6). The yellow band at R_f 0.25 gave 2-(ethoxycarbonyl)-3,5-dimethyl-1,4-benzoquinone (**7**, 96%): yellow needless, mp 46–47 °C; IR (CCl_4) 1745, 1660, 1235 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.37 (t, J = 7.1 Hz, 3 H), 2.06 (s, 3 H), 2.08 (d, J = 1.7 Hz, 3 H), 4.39 (q, J = 7.1 Hz, 2 H), 6.59 (q, J = 1.7 Hz, 1 H). Anal. Calcd for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81. Found: C, 63.54; H, 6.04. The spectral and physical data of **7** were in good agreement with those of the independently synthesized authentic sample as described below.

The band of R_f 0.05–0.2 gave 2-phenylethanol (**8**): 81%; colorless oil; IR (CCl_4) 3600, 3450, 2940, 1045, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.64 (br s, 1 H), 2.86 (t, J = 6.6 Hz, 2 H), 3.85 (t, J = 6.6 Hz, 2 H), 7.2–7.4 (m, 5 H). The spectral data of **8** agreed with those of authentic sample.

Preparation of 2-(Ethoxycarbonyl)-3,5-dimethyl-1,4-benzoquinone (7). 3,6-Dimethoxy-2,4-dimethylbenzoic acid, which was prepared from 2-acetyl-3,5-dimethylhydroquinone dimethyl ether by selective oxidation,[13] was ethylated by ethyl bromide and potassium carbonate in dry acetone. The resulting ethylated product was oxidized by CAN as same as described above. After worked up in the usual manner, the product was purified by TLC (C_6H_6), and the quinone **7** was obtained as yellow needles: 88% (from benzoic acid); mp 46–47 °C; IR (CCl_4) 1745, 1660, 1235 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.37 (t, J = 7.1 Hz, 3 H), 2.06 (s, 3 H), 2.08 (d, J = 1.7 Hz, 3 H), 4.39 (q, J = 7.1 Hz, 2 H), 6.59 (q, J = 1.7 Hz, 1 H).

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Table IV. Physical Properties of 4 and 5

product	mp, °C	elemental analysis or high-resolution MS: formula	atom	calcd	found	IR (CCl_4), cm^{-1}	^1H NMR ($CDCl_3$), δ (J, Hz)
4aM	oil	$C_{13}H_{16}O_4$		236.1048	236.1041	3610, 3450, 1715, 1620, 1220	1.38 (d, J = 7, 3 H), 2.28 (s, 3 H), 2.47 (s, 3 H), 3.26 (s, 3 H), 3.7–4.0 (m, 1 H), 4.29 (d, J = 3, 1 H), 4.58 (br s, 1 H), 6.75 (s, 1 H)
4aE	oil	$C_{14}H_{18}O_4$		250.1204	250.1186	3610, 3420, 1700, 1620, 1220	1.03 (t, J = 7, 3 H), 1.38 (d, J = 7, 3 H), 2.29 (s, 3 H), 2.47 (s, 3 H), 3.2–3.7 (m, 2 H), 3.75–4.15 (m, 1 H), 4.26 (d, J = 3, 1 H), 4.73 (br s, 1 H), 6.70 (s, 1 H)
4aP	oil	$C_{15}H_{20}O_4$		264.1361	264.1334	3620, 3400, 1715, 1620, 1285	0.91 and 1.06 (each d, J = 7, 6 H), 1.35 and 1.40 (each d, J = 7, 3 H), 2.32 (s, 3 H), 2.50 (s, 3 H), 3.61 (m, J = 6, 1 H), 4.03 (dq, J = 7 and 3, 1 H), 4.32 (d, J = 3, 1 H), 4.48 (s, 1 H), 6.79 (s, 1 H)
4aB	oil	$C_{16}H_{22}O_4$		278.1517	278.1497	3620, 3440, 1720, 1625, 1170	0.81 and 1.08 (each s, 9 H), 1.24 and 1.39 (each d, J = 6, 3 H), 2.32 (s, 3 H), 2.49 (s, 3 H), 4.12 (dq, J = 6 and 3, 1 H), 4.27 (d, J = 3, 1 H), 4.46 (s, 1 H), 6.78 (s, 1 H)
5aM	oil	$C_{13}H_{16}O_4$		236.1048	236.1046	3620, 3480, 1740, 1680, 1280	1.59 (dd, J = 7, 2, 3 H), 2.01 (s, 3 H), 2.11 (s, 3 H), 3.79 (s, 3 H), 4.93–5.26 (m, 1 H), 5.51 (s, 1 H), 6.17 (dd, J = 12, 2, 1 H), 6.48 (s, 1 H)
5aE	oil	$C_{14}H_{18}O_4$		250.1204	250.1186	3600, 3450, 1720, 1670, 1265	1.33 (t, J = 7, 3 H), 1.59 (dd, J = 7, 2, 3 H), 2.03 (s, 3 H), 4.29 (q, J = 7, 2 H), 4.93–5.27 (m, 1 H), 5.52 (s, 1 H), 6.20 (dd, J = 12, 2, 1 H), 6.48 (s, 1 H)
5aP	oil	$C_{15}H_{20}O_4$		264.1361	264.1365	3620, 3460, 1730, 1675, 1280	1.28 (d, J = 7, 6 H), 1.58 (dd, J = 7, 2, 3 H), 2.00 (s, 3 H), 2.10 (s, 3 H), 4.9–5.4 (m, 2 H), 5.30 (br s, 1 H), 6.19 (br d, J = 12, 2, 1 H), 6.45 (s, 1 H)
5aB	oil	$C_{16}H_{22}O_4$		278.1517	278.1494	3620, 3420, 1735, 1680, 1300	1.51 (s, 9 H), 1.58 (dd, J = 7, 2, 3 H), 2.00 (s, 3 H), 2.09 (s, 3 H), 4.9–5.4 (m, 1 H), 5.28 (br s, 1 H), 6.20 (br d, J = 13, 1 H), 6.42 (s, 1 H)
4bM	104–105	$C_{14}H_{18}O_4$		250.1205	250.1186	3430, 1700, 1610, 1460	1.16 (s, 3 H), 1.35 (s, 3 H), 2.25 (s, 3 H), 2.40 (s, 3 H), 3.17 (s, 3 H), 4.20 (s, 1 H), 5.40 (br s, 1 H), 6.61 (s, 1 H)
4bE	111–113	$C_{15}H_{20}O_4$		264.1361	264.1360	3475, 1685, 1610, 1140	1.12 (t, J = 7, 3 H), 1.16 (s, 3 H), 1.40 (s, 3 H), 2.27 (s, 3 H), 2.45 (s, 3 H), 3.47 (q, J = 7, 2 H), 4.35 (s, 1 H), 5.22 (s, 1 H), 6.68 (s, 1 H)
4bP	101–103	$C_{16}H_{22}O_4$		278.1518	278.1490	3610, 3470, 1710, 1470, 1170	1.04 (d, J = 6, 6 H), 1.15 (s, 3 H), 1.37 (s, 3 H), 2.28 (s, 3 H), 2.43 (s, 3 H), 3.87 (m, J = 6, 1 H), 4.18 (s, 1 H), 5.00 (br s, 1 H), 6.67 (s, 1 H)
4bB	99–102	$C_{17}H_{24}O_4$		292.1673	292.1652	3605, 3460, 1715, 1170	1.18 (s, 9 H), 1.40 (s, 3 H), 1.49 (s, 3 H), 2.29 (s, 3 H), 2.45 (s, 3 H), 4.14 (s, 1 H), 4.74 (br s, 1 H), 6.71 (s, 1 H)
5bM	oil	$C_{14}H_{18}O_4$		250.1205	250.1228	3620, 3460, 1735, 1280	1.65 (s, 6 H), 2.09 (s, 3 H), 2.18 (s, 3 H), 3.80 (s, 3 H), 4.51 (br s, 1 H), 6.02 (br s, 1 H), 6.48 (s, 1 H)
5bE	oil	$C_{15}H_{20}O_4$		264.1361	264.1363	3430, 1720, 1460, 1265, 1130	1.36 (t, J = 7, 3 H), 1.64 and 1.67 (each s, 6 H), 2.12 and 2.19 (each s, 6 H), 4.18 (q, J = 7, 2 H), 4.74 (br s, 1 H), 6.12 (s, 1 H), 6.61 (s, 1 H)
5bP	oil	$C_{16}H_{22}O_4$		278.1518	278.1509	3620, 1730, 1470, 1280, 1155	1.33 (d, J = 6, 6 H), 1.64 and 1.65 (each s, 6 H), 2.04 (s, 3 H), 2.12 (s, 3 H), 5.05 (br s, 1 H), 5.17 (m, J = 6, 1 H), 6.01 (s, 1 H), 6.42 (s, 1 H)
5bB	oil	$C_{17}H_{24}O_4$		292.1673	292.1645	3620, 1730, 1300, 1180	1.51 (s, 9 H), 1.62 and 1.65 (each s, 6 H), 1.99 (s, 3 H), 2.08 (s, 3 H), 4.99 (s, 1 H), 6.02 (br s, 1 H), 6.36 (s, 1 H)
4cM	161–164	$C_{19}H_{20}O_5$	C H	69.50 6.14	69.69 6.27	3380, 1680, 1605, 1250	2.25 (s, 3 H), 2.46 (s, 3 H), 3.16 (s, 3 H), 3.80 (s, 3 H), 4.49 (d, J = 2, 1 H), 4.73 (d, J = 2, 1 H), 5.07 (s, 1 H), 6.76 (s, 1 H), 6.94 (d, J = 8, 2 H), 7.41 (d, J = 8, 2 H)
4cE	146–148	$C_{20}H_{22}O_5$	C H	70.16 6.48	70.11 6.66	3400, 1700, 1610, 1240	0.99 (t, J = 7, 3 H), 2.26 (s, 3 H), 2.46 (s, 3 H), 3.13–3.48 (m, 1 H), 3.76 (s, 3 H), 4.32 (d, J = 2, 1 H), 4.73 (d, J = 2, 1 H), 5.53 (s, 1 H), 6.65 (s, 1 H), 6.80 (d, J = 8, 2 H), 7.32 (d, J = 8, 2 H)
4cP	107–110	$C_{21}H_{24}O_5$	C H	70.77 6.79	70.81 6.96	3620, 3450, 1715, 1620, 1255	0.91 and 0.97 (each d, J = 6, 6 H), 2.24 (s, 3 H), 2.45 (s, 3 H), 3.2–3.6 (m, 1 H), 3.73 (s, 3 H), 4.29 (d, J = 2, 1 H), 4.80 (d, J = 2, 1 H), 5.57 (br s, 1 H), 6.60 (s, 1 H), 6.74 (d, J = 8, 2 H), 7.27 (d, J = 8, 2 H)
4cB	144–147	$C_{22}H_{26}O_5$	C H	71.33 7.08	71.46 7.13	3605, 3440, 1710, 1615, 1255	0.93 (s, 9 H), 2.24 (s, 3 H), 2.44 (s, 3 H), 3.73 (s, 3 H), 4.35 (d, J = 2, 1 H), 4.97 (s, 1 H), 4.98 (d, J = 2, 1 H), 6.66 (s, 1 H), 6.80 (d, J = 8, 2 H), 7.33 (d, J = 8, 2 H)
4dM	193–195	$C_{19}H_{20}O_4$	C H	73.06 6.45	73.14 6.32	3380, 1685	2.21, 2.28, 2.34, 2.36, and 2.49 (each s, 9 H), 3.16 and 3.30 (each s, 3 H), 4.45–4.95 (m, 3 H), 6.65 and 6.77 (each s, 1 H), 6.95–7.45 (m, 4 H)
4dE	171–173	$C_{20}H_{22}O_4$	C H	73.60 6.79	73.41 6.96	3400, 1690, 1675	1.00 (t, J = 7, 3 H), 2.28 (s, 3 H), 2.34 (s, 3 H), 2.49 (s, 3 H), 3.41 (m, J = 7, 2 H), 4.49 (d, J = 2, 1 H), 4.71 (s, 1 H), 4.83 (d, J = 2, 1 H), 6.74 (s, 1 H), 7.18 (d, J = 8, 2 H), 7.36 (d, J = 8, 2 H)
4dP	146–149	$C_{21}H_{24}O_4$	C H	74.09 7.11	74.04 7.28	3610, 3440, 1710	0.93 and 0.97 (each d, J = 6, 6 H), 2.24 (s, 3 H), 2.31 (s, 3 H), 2.45 (s, 3 H), 3.45 (m, J = 6, 1 H), 4.43 (d, J = 2, 1 H), 4.89 (d, J = 2, 1 H), 5.02 (br s, 1 H), 6.67 (s, 1 H), 7.11 (d, J = 8, 2 H), 7.31 (d, J = 8, 2 H)
4dB	155–157	$C_{22}H_{26}O_4$	C H	74.55 7.39	74.39 7.48	3620, 3450, 1705	0.95 (s, 9 H), 2.25 (s, 3 H), 2.28 (s, 3 H), 2.44 (s, 3 H), 4.35 (d, J = 2, 1 H), 4.69 (s, 1 H), 4.97 (d, J = 2, 1 H), 6.65 (s, 1 H), 7.04 (d, J = 8, 2 H), 7.28 (d, J = 8, 2 H)

Table IV (Continued)

product	mp, °C	elemental analysis or high-resolution MS: formula	atom	calcd	found	IR (CCl_4), cm^{-1}	^1H NMR ($CDCl_3$), δ (J, Hz)
5dM	oil	$C_{19}H_{20}O_4$		312.1361	312.1393	3600, 3450, 1730, 1650, 1270, 1125	2.21 and 2.24 (each s, 6 H), 2.32 (s, 3 H), 3.90 (s, 3 H), 4.62 (s, 1 H), 6.20 (d, J = 13, 1 H), 6.73 (s, 1 H), 6.98 (d, J = 13, 1 H), 7.09 (d, J = 8, 2 H), 7.17 (d, J = 8, 2 H)
5dE	oil	$C_{20}H_{22}O_4$		326.1516	326.1479	3600, 3450, 1725, 1650, 1270, 1130	1.35 (t, J = 7, 3 H), 2.20 and 2.22 (each s, 6 H), 2.31 (s, 3 H), 4.37 (q, J = 7, 2 H), 4.88 (s, 1 H), 6.19 (d, J = 13, 1 H), 6.71 (s, 1 H), 6.95 (d, J = 13, 1 H), 7.08 (d, J = 8, 2 H), 7.15 (d, J = 8, 2 H)
5dP	oil	$C_{21}H_{24}O_4$		340.1674	340.1681	3610, 1725, 1650, 1275	1.30 (d, J = 6, 6 H), 2.12, 2.18, and 2.28 (each s, 9 H), 4.70 (br s, 1 H), 5.0–5.4 (m, J = 6, 1 H), 6.05 (d, J = 13, 1 H), 6.62 (s, 1 H), 6.91 (d, J = 13, 1 H), 6.9–7.2 (m, 4 H)
5dB	oil	$C_{22}H_{26}O_4$		354.1830	354.1830	3610, 1725, 1295	1.51 (s, 9 H), 2.15 (s, 6 H), 2.25 (s, 3 H), 4.74 (s, 1 H), 6.05 (d, J = 12, 1 H), 6.61 (s, 1 H), 6.89 (d, J = 12, 1 H), 7.0–7.2 (m, 4 H)
4eM	170–173	$C_{18}H_{18}O_4$	C H	72.47 6.08	72.43 6.19	3580, 3380, 1685, 1610, 1460	2.30 (s, 3 H), 2.55 (s, 3 H), 3.26 (s, 3 H), 4.51 (d, J = 2, 1 H), 4.76 (d, J = 2, 1 H), 4.80 (br s, 1 H), 6.76 (s, 1 H), 7.25–7.65 (m, 5 H)
4eE	152–155	$C_{19}H_{20}O_4$		312.1360	312.1355	3610, 3400, 1710, 1620	0.98 (t, J = 7, 3 H), 2.21 (s, 3 H), 2.41 (s, 3 H), 3.28 (m, 2 H), 4.29 (d, J = 2, 1 H), 4.73 (d, J = 2, 1 H), 5.20 (br s, 1 H), 6.60 (s, 1 H), 7.1–7.4 (m, 5 H)
4eP	136–138	$C_{20}H_{22}O_4$	C H	73.60 6.79	73.37 6.97	3620, 3400, 1715, 1625	0.96 and 0.99 (each d, J = 6, 6 H), 2.26 (s, 3 H), 2.46 (s, 3 H), 3.25–3.65 (m, J = 6, 1 H), 4.33 (d, J = 2, 1 H), 4.88 (d, J = 2, 1 H), 5.12 (br s, 1 H), 6.66 (s, 1 H), 7.10–7.35 (m, 5 H)
4eB	144–147	$C_{21}H_{24}O_4$	C H	74.09 7.11	73.93 7.17	3610, 1710	0.98 (s, 9 H), 2.29 (s, 3 H), 2.46 (s, 3 H), 4.27 (s, 1 H), 4.56 (s, 1 H), 4.98 (s, 1 H), 6.67 (s, 1 H), 7.1–7.5 (m, 5 H)
5eM	89–91	$C_{18}H_{18}O_4$	C H	72.47 6.08	72.38 6.34	3580, 3350, 1720, 1650, 1275	2.24 (s, 3 H), 2.27 (s, 3 H), 3.93 (s, 3 H), 4.62 (br s, 1 H), 6.28 (s, J = 13, 1 H), 6.81 (s, 1 H), 7.09 (d, J = 13, 1 H), 7.32 (s, 5 H)
5eE	oil	$C_{19}H_{20}O_4$	C H	73.06 6.45	72.91 6.35	3620, 3450, 1735, 1275	1.26 (t, J = 7, 3 H), 2.02 (s, 3 H), 2.08 (s, 3 H), 4.23 (q, J = 7, 2 H), 5.37 (br s, 1 H), 6.00 (d, J = 13, 1 H), 6.52 (s, 1 H), 6.86 (d, J = 13, 1 H), 7.08 (s, 5 H)
5eP	oil	$C_{20}H_{22}O_4$	C H	73.60 6.79	73.37 6.97	3620, 1730, 1290	1.31 (d, J = 6, 6 H), 2.09 (s, 3 H), 2.17 (s, 3 H), 5.10 (br s, 1 H), 4.96–5.37 (m, J = 6, 1 H), 6.06 (d, J = 13, 1 H), 6.58 (s, 1 H), 6.94 (d, J = 13, 1 H), 7.14 (s, 5 H)
5eB	oil	$C_{21}H_{24}O_4$	C H	74.09 7.11	73.64 7.23	3620, 1730, 1295	1.52 (s, 9 H), 2.09 (s, 3 H), 2.15 (s, 3 H), 5.04 (br s, 1 H), 6.06 (d, J = 13, 1 H), 6.56 (s, 1 H), 6.96 (d, J = 13, 1 H), 7.15 (s, 5 H)
4fM	203–205	$C_{18}H_{17}O_4Cl$	C H	64.97 5.15	64.92 4.93	3380, 1680, 1605	2.17 (s, 3 H), 2.28 (s, 3 H), 3.25 (s, 3 H), 4.47 (br s, 1 H), 4.63 (d, J = 2, 1 H), 4.81 (d, J = 2, 1 H), 6.52 (s, 1 H), 7.02–7.38 (m, 4 H)
4fE	147–152	$C_{19}H_{19}O_4Cl$	C H	65.80 5.52	65.82 5.59	3400, 1675	1.01 (t, J = 7, 3 H), 2.28 (s, 3 H), 2.48 (s, 3 H), 3.18–3.53 (m, 2 H), 4.44 (d, J = 2, 1 H), 4.59 (s, 1 H), 4.81 (d, J = 7, 1 H), 6.71 (s, 1 H), 7.33 (s, 4 H)
4fP	140–144	$C_{20}H_{21}O_4Cl$	C H	66.57 5.87	66.83 5.96	3620, 3440, 1705	0.94 and 0.98 (each d, J = 6, 6 H), 2.28 (s, 3 H), 2.46 (s, 3 H), 3.25–3.65 (m, J = 6, 1 H), 4.31 (d, J =2, 1 H), 4.86 (d, J = 2, 1 H), 5.18 (br s, 1 H), 6.65 (s, 1 H)
4fB	oil	$C_{21}H_{23}O_4Cl$	C H	67.29 6.19	67.26 6.28	3620, 3400, 1710	0.95 (s, 9 H), 2.28 (s, 3 H), 2.43 (s, 3 H), 4.23 (d, J = 2, 1 H), 4.64 (br s, 1 H), 4.95 ns, 1 H), 6.65 (s, 1 H), 7.1–7.4 (m, 4 H)
5fM	135–137	$C_{18}H_{17}O_4Cl$	C H	64.97 5.15	64.91 4.95	3580, 3350, 1720, 1650, 1275	2.16 (s, 3 H), 2.20 (s, 3 H), 3.82 (s, 3 H), 4.69 (s, 1 H), 6.05 (d, J = 13, 1 H), 6.63 (s, 1 H), 6.90 (d, J = 13, 1 H), 7.09 (s, 5 H)
5fE	87–88	$C_{19}H_{19}O_4Cl$	C H	65.80 5.52	65.65 5.43	3580, 1720	1.32 (t, J = 7, 3 H), 2.16 (s, 3 H), 2.18 (s, 3 H), 4.32 (q, J = 7, 2 H), 5.01 (br s, 1 H), 6.05 (d, J = 13, 1 H), 6.63 (s, 1 H), 6.93 (d, J = 13, 1 H), 7.10 (s, 4 H)
5fP	oil	$C_{20}H_{21}O_4Cl$	C H	66.57 5.87	66.58 5.72	3620, 1735	1.22 (d, J = 6, 6 H), 2.09 (s, 3 H), 2.17 (s, 3 H), 5.11 (s, 1 H), 5.0–5.4 (m, 1 H), 6.00 (d, J = 13, 1 H), 6.57 (s, 1 H), 6.93 (d, J = 13, 1 H), 7.14 (s, 4 H)
5fB	164–166	$C_{21}H_{23}O_4Cl$	C H	67.29 6.19	67.27 6.02	3620, 1730	1.50 (s, 9 H), 2.15 (s, 6 H), 4.72 (br s, 1 H), 6.01 (d, J = 13, 1 H), 6.80 (s, 1 H), 6.93 (d, J = 13, 1 H), 7.08 (s, 4 H)
4gM	oil	$C_{18}H_{17}NO_6$		343.1055	343.1054	3600, 3370, 1710, 1620, 1535, 1360	2.29 (s, 3 H), 2.50 (s, 3 H), 3.20 (s, 3 H), 4.50 (d, J = 2, 1 H), 4.72 (br s, 1 H), 4.86 (d, J = 2, 1 H), 6.77 (s, 1 H), 7.58 (t, J = 8, 1 H), 7.81 (d, J = 8, 1 H), 8.23 (d, J = 8, 1 H), 8.37 (br s, 1 H)
4gE	oil	$C_{19}H_{19}NO_6$		357.1211	357.1174	3600, 1700, 1525, 1350	1.03 (t, J = 7, 3 H), 2.29 (s, 3 H), 2.48 (s, 3 H), 3.2–3.6 (m, 2 H), 4.41 (d, J = 2, 1 H), 4.90 (d, J = 2, 1 H), 4.95 (br s, 1 H), 6.72 (s, 1 H), 7.51 (t, J = 8, 1 H), 7.76 (d, J = 8, 1 H), 8.16 (d, J = 8, 1 H), 8.30 (br s, 1 H)
5gM	oil	$C_{18}H_{17}NO_6$	C H N	62.97 4.99 4.08	63.20 4.95 4.05	3580, 3350, 1720, 1650, 1525, 1350	2.18 (s, 3 H), 2.23 (s, 3 H), 3.88 (s, 3 H), 5.15 (br s, 1 H), 6.18 (d, J = 13, 1 H), 6.73 (s, 1 H), 7.17 (d, J = 13, 1 H), 7.38 (t, J = 8, 1 H), 7.53 (d, J = 8, 1 H), 7.97 (d, J = 8, 1 H), 8.07 (br s, 1 H)

Table IV (Continued)

product	mp, °C	elemental analysis or high-resolution MS: formula	atom	calcd	found	IR (CCl_4), cm^{-1}	^1H NMR ($CDCl_3$), δ (J, Hz)
5gE	oil	$C_{19}H_{19}NO_6$		357.1211	357.1218	3580, 3350, 1715, 1655, 1525, 1345	1.31 (t, J =7, 3 H), 2.15 (s, 3 H), 2.18 (s, 3 H), 4.32 (q, J = 7, 2 H), 5.22 (br s, 1 H), 6.11 (d, J = 13, 1 H), 6.66 (s, 1 H), 7.11 (d, J = 13, 1 H), 7.31 (t, J = 8, 1 H), 7.46 (d, J = 8, 1 H), 7.91 (d, J = 8, 1 H), 8.00 (br s, 1 H)
5gP	oil	$C_{20}H_{21}NO_6$		371.1367	371.1325	3620, 3460, 1735, 1660, 1540, 1360	1.31 (d, J = 7, 6 H), 2.20 (s, 3 H), 2.24 (s, 3 H), 4.89 (br s, 1 H), 5.27 (m, J = 7, 1 H), 6.16 (d, J = 13, 1 H), 6.73 (s, 1 H), 7.18 (d, J = 13, 1 H), 7.40 (t, J = 8, 1 H), 7.52 (d, J = 8, 1 H), 8.01 (d, J = 8, 1 H), 8.09 (br s, 1 H)
5gB	oil	$C_{21}H_{23}NO_6$		385.1523	385.1502	3620, 3450, 1730, 1660, 1535, 1365	1.51 (s, 9 H), 2.22 (s, 6 H), 4.66 (br s, 1 H), 6.15 (d, J = 13, 1 H), 6.71 (s, 1 H), 7.18 (d, J = 13, 1 H), 7.3–7.6 (m, 2 H), 7.9–8.2 (m, 2 H)

Preparation of 2-*p*-Anisylidene-5-methoxy-4,6-dimethylbenzofuran-3(2*H*)-one (11c). This compound was prepared by the modified method of Hutchins[11] in the following way. Quinone **1c** was reduced by $Na_2S_2O_4$ and acetylated with acetic anhydride and pyridine to hydroquinone diacetate of **1c**. The diacetate was bromintaed with Br_2 in chloroform. To a hot ethanol solution of the resulting bromide was added an aqueous 3 M NaOH solution. After cooling, the reaction mixture was diluted with water and acidified, and then the products were extracted with chloroform. The chloroform extract was dried and evaporated in vacuo. The resulting yellow product was purified by column chromatography ($CHCl_3$) and recrystallized from benzene–hexane to give 2-*p*-anisylidene-5-hydroxy-4,6-dimethylbenzofuran-3-(2*H*)-one (**10c**): 54%; yellow microcrystal, mp 206–207 °C; IR ($CHCl_3$) 3600, 1685, 1642, 1600, 1505, 1250, 1162 cm^{-1}; ^1H NMR ($CDCl_3$–CD_3COCD_3) δ 2.34 (s, 3 H), 2.54 (s, 3 H), 3.81 (s, 3 H), 6.62 (s, 1 H), 6.89 (s, 1 H), 6.92 (d, J = 8 Hz, 2 H), 7.81 (d, J = 8 Hz, 2 H).

The synthesized **10c** was methylated by methyl iodide and potassium carbonate in acetone. The resulting methyl ether **11c** was purified by TLC ($CHCl_3$) and recrystallized from benzene–hexane to give yellow needles: 71%; mp 157–158.5 °C; IR (CCl_4) 1702, 1650, 1602, 1512, 1245 cm^{-1}; ^1H NMR (CCl_4) δ 2.37 (s, 3 H), 2.60 (s, 3 H), 3.70 (s, 3 H), 3.83 (s, 3 H), 6.73 (s, 1 H), 6.91 (s, 1 H), 6.94 (d, J = 8 Hz, 2 H), 7.83 (d, J = 8 Hz, 2 H). Anal. Calcd for $C_{19}H_{18}O_4$: C, 73.53; H, 5.85. Found: C, 73.43; H, 6.06.

Preparation of 6-Methoxy-3,5,7-trimethylchromone (14a). Trimethylchromone **14a** was synthesized by the modified method of Venkataraman[12] in the following manner. To sodium metal in a flask cooled in an ice–water bath was added an ethyl formate solution of 6′-hydroxy-3′-methoxy-2′,4′-dimethylpropiophenone, which was prepared by selective demethylation of 3′,6′-dimethoxy-2′,4′-dimethylpropiophenone with $AlCl_3$, and stirred to room temperature for overnight. The reaction mixture was quenched with water, acidified with 6 M HCl, and extracted with benzene. The benzene extract was dried (Na_2SO_4) and evaporated in vacuo. The resulting oil was 2-hydroxy-6-methoxy-3,5,7-trimethylchroman-4-one: IR (CCl_4) 3605, 3440, 1695, 1615, 1470, 1245 cm^{-1}; ^1H NMR (CCl_4) δ 1.14 (d, J = 7 Hz, 3 H), 2.16 (s, 3 H), 2.40 (s, 3 H), 2.55–2.90 (m, 1 H), 3.52 (s, 3 H), 4.60 (br s, 1 H), 5.17 and 5.48 (each d, J = 6 and 4 Hz, 1 H), 6.43 and 6.47 (each s, 1 H).

The above hydroxychromanone was dissolved in acetic acid and refluxed for 30 min for dehydration. The reaction mixture was worked up as usual way. The resulting product was purified by TLC (C_6H_6), and the desired trimethylchromone **14a** was obtained as colorless oil: 63%; IR (CCl_4) 1655, 1612, 1465, 1165 cm^{-1}; ^1H NMR (CCl_4) δ 1.81 (s, 3 H), 2.24 (s, 3 H), 2.60 (s, 3 H), 3.56 (s, 3 H), 6.78 (s, 1 H), 7.42 (s, 1 H); MS, for $C_{13}H_{14}O_3$ m/e 218.0940 (*theory* 218.0942).

Photochemical Reaction of 1e in an Ethanol–Benzene Mixture. A solution of **1e** (0.3 mmol) in 30 mL of an benzene–ethanol (appropriate proportion) mixture was irradiated for 1 h under the same conditions. After reaction, the solvent was removed under reduced pressure, and the resulting oil was separated by TLC ($CHCl_3$–C_6H_6) into recovered **1e** and a mixture of **4eE** and **5eE**. The yields of **4eE** and **5eE** were determined by ^1H NMR spectroscopy. The resulting data are shown in Figure 1.

Photochemical Reactions of 1e in Several Solvents. The reactions of **1e** in several solvents were carried out under the same conditions in alcohols. The reactions of **1e** in benzene, acetonitrile, and acetone gave only the starting quinone, all in 99% yields.

Irradiation of **1e** in benzene containing methanol (4%) for 1 h gave **1e** (51%), **5eM** (48%), and trace amounts of **4eM**.

After irradiation of **1e** in benzene containing acetic acid (6%) for 1 h, the solvent was removed as complete as possible under reduced pressure. The residue was chromatographed on column. The first yellow component was recovered **1e** (8%), the second yellow component was 2-benzylidene-5-hydroxy-4,6-dimethylbenzofuran-3(2*H*)-one (**10e**, 17%, a mixture of *E* and *Z* isomers; ca. 1:2), which was isolated *E* and *Z* isomers after acetylation, the third was 3-hydroxy-2,4-dimethyl-6-(styryloxy)benzoic acid (**5eH**, R = H; 38%) which was probably hydrolysis product of acetic 3-hydroxy-2,4-dimethyl-6-(styryloxy)benzoic anhydride (**5eA**; R = Ac), and the fourth was 2-(α-acetoxybenzyl)-5-hydroxy-4,6-dimethylbenzofuran-3(2*H*)-one (**4eA**, R = Ac; 35%).

Acetate of (*E*)-**10e**: yellow solid, mp 177–180 °C; IR ($CHCl_3$) 1760, 1690, 1605, 1195 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.21 (s, 3 H), 2.30 (s, 3 H), 2.43 (s, 3 H), 6.85 (s, 2 H), 7.3–7.5 (m, 3 H), 8.0–8.25 (m, 2 H). Anal. Calcd for $C_{19}H_{16}O_4$: C, 74.01; H, 5.23. Found: C, 74.07; H, 5.19.

Acetate of (*Z*)-**10e**: yellow prisms, mp 203–204 °C; IR ($CHCl_3$) 1760, 1705, 1650, 1615, 1200 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.24 (s, 3 H), 2.32 (s, 3 H), 2.45 (s, 3 H), 6.78 (s, 1 H), 7.01 (s, 1 H), 7.3–7.6 (m, 3 H), 7.8–8.0 (m, 2 H). Anal. Calcd for $C_{19}H_{16}O_4$: C, 74.01; H, 5.23. Found: C, 74.00; H, 5.21.

4eA (a mixture of diastereoisomers; 45:55): IR (CCl_4) 3610, 3490, 1755, 1715, 1620, 1220 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.91, 2.11, 2.28, 2.32, and 2.43 (each s, 9 H), 4.65 and 4.84 (each d, J = 3.5 Hz, 1 H), 6.21 (d, J = 3.5 Hz, 1 H), 6.63 and 6.77 (each s, 1 H), 7.1–7.6 (m, 6 H). Anal. Calcd for $C_{19}H_{18}O_5$: C, 69.93; H, 5.56. Found: C, 70.05; H, 5.60.

5eH: oil; IR ($CHCl_3$) 3600, 3500–2450, 1710, 1130 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.24 (s, 3 H), 2.29 (s, 3 H), 5.55 (br s, 2 H), 6.28 (d, J = 13 Hz, 1 H), 6.79 (s, 1 H), 7.08 (d, J = 13 Hz, 1 H), 7.28 (s, 5 H). The product **5eH** was identified to convert it by the methylation with diazomethane to **5eM**.

Photochemical Reaction of 15. The reaction of **15** in *tert*-butyl alcohol was carried out under the same conditions as described above for **1**. The obtained crude reacton products were chromatographed on column. The first yellow component was recovered **15** (5%), the second was the hydroquinone of **15** (1%), the third was *tert*-butyl 5-hydroxy-4-methyl-2-[(α-methylstyryl)oxy]benzoate (**19B**, 21%), the fourth was 2-(α-*tert*-butoxybenzyl)-5-hydroxy-2,6-dimethylbenzofuran-3(2*H*)-one (**17B**, 4%), which shoed also the similar fluorescence as **4** when it was exposed to ultraviolet light on TLC, and the fifth was a mixture of chromone derivatives **21** and **24**. These chromones were separated as 6-methoxy-2,7-dimethyl-3-phenylchromone (**22**, 44%) and 6-methoxy-3,7-dimethyl-2-phenylchromone (**25**, 24%) after the methylation.

17B (a mixture of diastereoisomers; ca. 3:1): IR ($CHCl_3$) 3350, 1685, 1460, 1195 cm^{-1}; ^1H NMR (CCl_4) δ 0.88 and 1.22 (each s, 9 H), 1.14 and 1.51 (each s, 3 H), 2.20 and 2.31 (each s, 3 H), 3.68 and 4.76 (each s, 1 H), 6.06 (br s, 1 H), 6.80 and 6.95 (each s, 1 H), 7.2–7.6 (m, 6 H); MS for $C_{21}H_{24}O_4$ m/e 340.1638 (theory 340.1672).

19B (a mixture of cis and trans isomers; ca. 2:3): IR (CCl_4) 3430, 1680, 1410, 1190 cm^{-1}; ^1H NMR (CCl_4) δ 1.42 and 1.49 (each s, 9 H), 1.82, 2.09, 2.14, and 2.18 (each s, 6 H), 5.24 and 5.42 (each s, 1 H), 6.63 and 6.70 (each s, 1 H), 6.9–7.1 (m, 5 H), 7.35–7.5 (m, 2 H); MS, for $C_{21}H_{24}O_4$ m/e 340.1674 (theory 340.1672).

22: colorless prisms, mp 130–132 °C; IR (CCl_4) 1645, 1470, 1425 cm^{-1}; ^1H NMR (CCl_4) δ 2.20 (s, 3 H) 2.27 (s, 3 H), 3.88 (s, 3 H), 7.0–7.5 (m, 7 H). Anal. Calcd for $C_{18}H_{16}O_3$: C, 77.12; H, 5.57. Found: C, 76.85; H, 5.71.

25: colorless prisms, mp 153–155 °C; IR (CCl_4) 1630, 1470, 1425 cm^{-1}; ^1H NMR (CCl_4) δ 2.03 (s, 3 H), 2.26 (s, 3 H), 3.86 (s, 3 H), 7.14 (s, 1 H), 7.4–7.7 (m, 6 H). Anal. Calcd for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75. Found: C, 77.22; H, 5.75.

The syntheses of **22** and **25** by another route were reported in the previous paper.[9]

The reaction of **15** in acetone was also carried out under the same conditions. After removal of the solvent the residue was chromatographed on column with benzene as eluent. The first yellow component was recovered **15** (a mixture of cis and trans isomers, 81%), and the residue was eluted by ether. The ether eluent was further chromatographed on TLC ($CHCl_3$ containing 15% AcOEt). The colorless band at R_f 0.2 was chromone derivative **24** (16%), which was methylated to **25**.

After irradiation of **15** in acetone containing water (9%) under the same conditions, the solvent was removed under reduce pressure, and then the reaction products were extracted with chloroform from the residual water mixture. The extract was chromatographed on column (C_6H_6). The first yellow compound was recovered **15** (18%), and the residue was eluted by ether. The ether eluent was chromatographed on TLC ($CHCl_3$ containing 15% AcOEt). The colorless band at R_f 0.2 was a mixture of **21** (18%) and **24** (28%), which were determined after methylation, the fluorescence band (under expose to UV lamp) at R_f 0.1 was 5-hydroxy-2-(α-hydroxybenzyl)-2,6-dimethylbenzofuran-3(2*H*)-one (**17H**, 19%), and the origin was 5-hydroxy-4-methyl-2-[(α-methylstyryl)oxy]benzoic acid (**19H**, 13%).

17H: colorless solid, mp 153–154 °C; IR ($CHCl_3$) 3600, 3320, 1695, 1470 cm^{-1}; ^1H NMR ($CDCl_3$ + CD_3COCD_3) δ 1.22 (s, 3 H), 2.31 (s, 3 H), 3.57 (d, J = 6 Hz, 1 H), 4.95 (d, J = 6 Hz, 1 H), 6.98 (s, 1 H), 7.05 (s, 1 H), 7.3–7.65 (m, 5 H), 7.98 (s, 1 H). Anal. Calcd for $C_{17}H_{16}O_4$: C, 71.82; H, 5.67. Found: C, 72.02; H, 5.44.

19H (a mixture of cis–trans isomers; ca. 1:1): colorless oil; ^1H NMR (CCl_4) δ 2.00, 2.15, 2.23, and 2.28 (each s, 6 H), 6.08 and 6.18 (each s, 1 H), 6.85 and 6.95 (each s, 1 H), 7.15–7.6 (m, 7 H), 7.74 and 7.76 (each s, 1 H). **19H** was identified to convert it by the methylation with diazomethane to methyl 5-hydroxy-4-methyl-2-[(α-methylstyryl)oxy]benzoate (**19M**; a mixture of cis–trans isomers): colorless needles, mp 131–133 °C; IR ($CHCl_3$) 3400, 1710 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.89, 2.19, 2.21, and 2.27 (each s, 6 H), 3.83 and 3.89 (each s, 3 H), 5.54 and 6.75 (each s, 1 H), 6.19 (br s, 1 H), 6.86 and 6.97 (each s, 1 H), 7.05–7.75 (m, 6 H). Anal. Calcd for $C_{18}H_{18}O_4$: C, 72.47; H, 6.08. Found: C, 72.56; H, 6.01.

Acknowledgment. I am sincerely grateful to Professor K. Maruyama of Kyoto University for his continuing interest and useful suggestions, and I thank Drs. O. Soga and A. Takuwa for encouragement during this work.

Registry No. **1a**, 92777-31-6; **1b**, 92777-26-9; **1c**, 92777-27-0; **1d**, 92777-28-1; **1e**, 92777-29-2; **1f**, 92777-30-5; **1g**, 92777-31-6; **4aM**, 92777-45-2; **4aE**, 113008-35-8; **4aP**, 113008-36-9; **4aB**, 113008-37-0; **4bM**, 92777-47-4; **4bE**, 92777-34-9; **4bP**, 113008-38-1; **4bB**, 113008-39-2; **4cM**, 92777-48-5; **4cE**, 92777-35-0; **4cP**, 113008-40-5; **4cB**, 113008-41-6; **4dM**, 92777-49-6; **4dE**, 92777-36-1; **4dP**, 113008-42-7; **4dB**, 113008-43-8; **4eM**, 92777-50-9; **4eE**, 92777-37-2; **4eP**, 113008-44-9; **4eB**, 113008-45-0; **4eA**, 113008-79-0; **4fM**, 92777-52-1; **4fE**, 92777-39-4; **4fP**, 113008-46-1; **4fB**, 113008-47-2; **4gM**, 92777-53-2; **4gE**, 92777-41-8; **4gP**, 113008-48-3; **5aM**, 92777-46-3; **5aE**, 92777-32-7; **5aP**, 113008-49-4; **5aB**, 113008-50-7; **5bM**, 113008-51-8; **5bE**, 92777-33-8; **5bP**, 113008-52-9; **5bB**, 113008-53-0; **5dM**, 113008-54-1; **5dE**, 113008-55-2; **5dP**, 113008-56-3; **5dB**, 113008-57-4; **5eM**, 92777-51-0; **5eE**, 92777-38-3; **5eP**, 113008-58-5; **5eB**, 113008-59-6; **5eH**, 113008-78-9; **5fM**, 92777-20-3; **5fE**, 92777-40-7; **5fP**, 113008-60-9; **5fB**, 113008-61-0; **5gM**, 92777-19-0; **5gE**, 92777-42-9; **5gP**, 113008-62-1; **5gB**, 113008-63-2; **6**, 92812-34-5; **7**, 113008-75-6; **8**, 60-12-8; **10c**, 113008-64-3; **10d**, 113008-66-5; **10e**, 113008-77-8; (*E*)-**10e** acetate, 113008-80-3; (*Z*)-**10e** acetate, 113008-81-4; **11c**, 113008-65-4; **11d**, 113008-67-6; **13a**, 98231-01-7; **13e**, 113008-68-7; **13f**, 113008-69-8; **14a**, 113034-68-7; **14f**, 113008-70-1; **15**, 98230-47-8; **15** hydroquinone, 98230-54-7; **17B**, 113008-83-6; **17H**, 113008-84-7; **19M**, 113008-86-9; **19B**, 113008-82-5; **19H**, 113008-85-8; **21**, 98230-52-5; **22**, 98230-69-4; **24**, 98230-53-6; **25**, 98230-70-7; MeOH, 67-56-1; EtOH, 64-17-5; *i*-PrOH, 67-63-0; *t*-BuOH, 75-65-0; 2-(α-ethoxybenzyl)-5-hydroxy-4,6-dimethylbenzofurane, 92777-43-0; 5-acetoxy-2-(α-ethoxybenzyl)-4,6-dimethylbenzofuran, 113008-71-2; 3-methoxy-2,4-dimethyl-6-(styryloxy)benzyl alcohol, 113008-72-3; 3-methoxy-2,4-dimethyl-6-(styryloxy)benzyl acetate, 113008-73-4; ethyl 3-acetoxy-2,4-dimethyl-6-phenethylbenzoate, 113008-74-5; 2-hydroxy-6-methoxy-3,5,7-trimethylchroman-4-one, 113008-76-7.

Structure of Rearrangement Products Obtained on Treatment of 19-Hydroxyandrost-4-ene-3,17-dione under Epoxidation Conditions

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Received August 19, 1987

Treatment of 19-hydroxyandrost-4-ene-3,17-dione (**2**) with hydrogen peroxide in alkaline methanol at 0–4 °C for 60–90 min gave the corresponding 4β,5β-epoxide **4** in good yield. However, with a reaction period of 16 h and at 21 °C, only traces of the 4β,5β-epoxide **4** were obtained and a 20% yield of a second product was isolated. The structure of this product was determined by X-ray crystallography and found to be 19-(hydroperoxymethyl)-4β,5-epoxy-2-oxa-5β,10α-androstane-3,17-dione (**5**). The reactions of this hydroperoxide with hydrogen bromide, sodium iodide, and methyl iodide were examined. Under slightly different reaction conditions, the 3,5-seco compound **16** was isolated.

In connection with our studies on the active site of a 17β-hydroxy steroid dehydrogenase, 4,19-dihydroxyandrost-4-ene-3,17-dione (**8**) was required as a substrate for affinity labeling experiments. The synthesis of the

0022-3263/88/1953-1515$01.50/0