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Photoinduced Intramolecular Cyclization Reaction of 3-Substituted 2-Alkenoyl-1,4-benzoquinones

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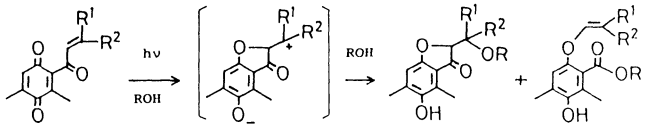
Irradiation of 3-alkoxy-2-alkenoyl-1,4-benzoquinones in solution gave tricyclic compounds (5*H*-pyrano[4,3,2-*de*][1,3]benzodioxin derivatives) and 3-alkylthio-2-alkenoyl-1,4-benzoquinones gave similar products (5*H*-pyrano[4,3,2-*de*][3,1]benzoxathiin derivatives). Each reaction initiates via γ-hydrogen abstraction by photoexcited quinone to produce diradical intermediates which intramolecularly cyclize to give the products.

Such isoprenoid 1,4-quinones as plastoquinone, ubiquinone, and menaquinone have been well known to play important roles in nature,[1] e.g. in processes such as electron transport and oxidative phosphorylation. The photochemical reactions of related quinone compounds, therefore, have been extensively investigated under several conditions.[2] For example, irradiation of isoprenoid 1,4-quinones under aerobic conditions gives trioxane and hydroperoxide, but that of the quinones under anaerobic conditions gives dihydrobenzofuran, chromene, or dimer.[2] Chlorobiumquinone,[3] which is an alkenoyl-1,4-quinone with both an olefinic double bond and a carbonyl group in the side chain, was isolated from a natural source. An investigation of the photochemical reactions of 2-alkenoyl-1,4-benzoquinones **1** is, therefore, of interest from both biological and photochemical points of view.



1 **2** **3** **4** (1)

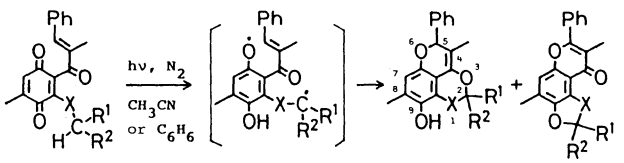
It has been reported that irradiation of alkenoyl quinones **1** in benzene under aerobic conditions affords relatively stable cyclic peroxides.[4] Recently, we reported the photochemical reaction of **1** in alcohols under anaerobic conditions to give two isomeric adducts (**3** and **4**)[5] via a zwitterionic intermediate **2** (Eq. 1). Afterwards, we preliminarily reported that 2-alkenoyl-3-alkoxy-1,4-benzoquinones (**5G**) reacted photochemically to give intramolecular cyclization products, 5*H*-pyrano[4,3,2-*de*][1,3]benzodioxin derivatives (**7G**),[6] via γ-hydrogen abstraction (Eq. 2). The photoinduced γ-hydrogen abstraction of alkoxyquinones[7] or the intramolecular cyclization reaction of 2-alkenyl-3-alkoxy-1,4-quinone,[8] and the intermolecular photochemical reaction of alkoxyquinones with olefins[9] have been extensively investigated so far.

In this paper, we describe the photochemical reaction of alkoxybenzoquinones **5G** and 2-alkenoyl-3-alkylthio-1,4-benzoquinones (**5S**) which are noticeably different from that of other alkoxyquinones; the quinones **5G** gave intramolecularly cyclized products **7G**, and **5S** gave similar cyclization products, 5*H*-pyrano[4,3,2-*de*][3,1]benzoxathiin derivatives (**7S**), in high yields together with minor products, 9*H*-[1,3]oxathiolo[4,5-*f*][1]-benzopyran-9-one derivatives (**8S**)[10] (Eq. 2).

Results and Discussion

Photochemical Reaction of 5G in Acetonitrile. When a solution of 3-methoxy-5-methyl-2-(α-methylcinnamoyl)-1,4-benzoquinone (**5Ga**) in acetonitrile (0.01 mol dm^{-3}) was irradiated with light at wavelengths longer than 410 nm under a nitrogen atmosphere for 3 h, an intramolecularly cyclized product, 4,8-dimethyl-5-phenyl-5*H*-pyrano[4,3,2-*de*][1,3]benzodioxin-9-ol (**7Ga**), was obtained as the major product in 50% yield. The structure of **7Ga** was elucidated by its spectral data and chemical transformation, as reported in a previous paper.[6] Similarly, other alkoxyquinones **5Gb—f** reacted under the same conditions to give **7Gb—f** in reasonable yields. All of the products **7Gb—f**, except **7Gd**, were mixtures of diastereoisomers. In the case of **7Gb**, the diastereoisomers were separated by TLC into each isomer after acetylation.

On the other hand, in the cases of the reaction of **5Gd** and **5Ge**, other minor products, **8Gd** and **8Ge**,[11] were respectively obtained, even though in low yields. The results are summarized in Table 1. The relative



5G (X=O) **6G** **7G** **8G**
5S (X=S) **6S** **7S** **8S**

a: $R^1=R^2=H$; b: $R^1=H$, $R^2=Me$; c: $R^1=H$, $R^2=Et$; d: $R^1=R^2=Me$; e: $R^1=Me$, $R^2=Et$; f: $R^1=H$, $R^2=Ph$ (2)

Table 1. Photochemical Reaction of 5[a]

Quinone	Substituents		Yields of products/%[b]	
	R^1	R^2	7	8
5Ga	H	H	50[c]	0
5Gb	H	Me	75	0
5Gc	H	Et	81	0
5Gd	Me	Me	77	5
5Ge	Me	Et	72	8
5Gf	H	Ph	81	0
5Sb	H	Me	75	15
5Sc	H	Et	70	17
5Sd	Me	Me	80	7
5Se	Me	Et	89	7
5Sf	H	Ph	66	24
5Sg	$XCHR^1R^2$=SBu^t		0[d]	0[d]

a) Acetonitrile was used for **5G** and benzene was used for **5S**. b) Isolated yields based on the quinone used. Hydroquinones of **5S** were obtained as another minor products. The recovered quinones were mostly under 10 per cent for **5G** and were nothing for **5S**. c) **5Ga** was recovered in a 31% yield. d) **5Sg** was almost recovered.

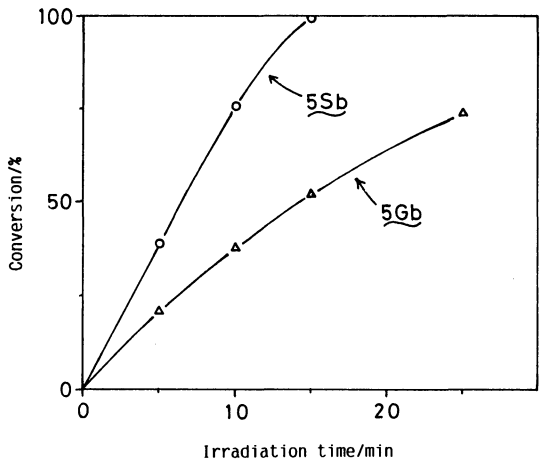
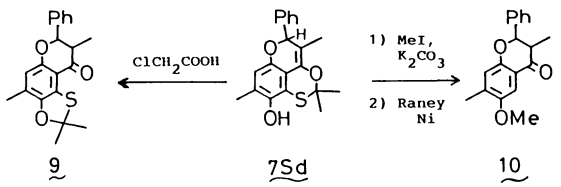


Fig. 1. Comparison of the photoreactivity of **5Gb** and **5Sb**. These reactions were carried out in $CDCl_3$ (ca. 0.026 mol dm^{-3}) and the conversion of quinones was determined by the use of ^{1}H NMR spectrometer.

reactivity of **5Ga**, **b**, and **d** having methoxyl, ethoxyl, and isopropoxyl groups increases in this order by 1:2:3.[6]

From these results, as depicted in Eq. 2, the reaction could proceed through γ-hydrogen abstraction by excited quinone carbonyl. Probably the resulting diradical **6G** intramolecularly attacks the carbonyl oxygen in the alkenoyl side chain, and finally cyclizes to give **7G**. This sort of bicyclo-cyclization reaction initiated by γ-hydrogen abstraction is quite novel.

Photochemical Reaction of 5S in Benzene. Irradiation of 3-isopropylthio-5-methyl-2-(α-methylcinnamoyl)-1,4-benzoquinone (**5Sd**) in benzene for 1.5 h under the same conditions as described in the reaction of **5G** gave two cyclization products, 2,2,4,8-tetramethyl-5-phenyl-5*H*-pyrano[4,3,2-*de*][3,1]benzoxathiin-9-ol (**7Sd**, 80%) and 2,2,4,8-tetramethyl-7-phenyl-9*H*-[1,3]oxathiolo[4,5-*f*][1]benzopyran-9-one (**8Sd**, 7%).[10] The structure of **7Sd** was elucidated by its spectral data. The ^{1}H NMR data of **7Sd** showed similar signal patterns to that of **7Gd**; for instance, **7Sd** showed four singlet peaks at δ 1.60, 1.64, 1.78, and 2.10 due to four methyl groups, three singlet peaks at δ 4.52, 5.57, and 6.24 due to hydroxyl, methine, and aromatic protons, and one singlet peak at δ 7.27 due to a phenyl group. The structure of **7Sd** was further confirmed by chemical derivations with chloroacetic acid to 2,2,4,8-tetramethyl-7-phenyl-7,8-dihydro[1,3]-oxathiolo[4,5-*f*][1]benzopyran-9-one (**9**, 63%) and by



9 7Sd 10 (3)

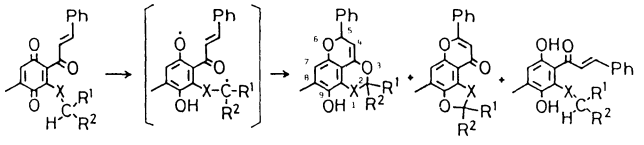
the oxidation of **7Sd** with chloranil to give a stable product **8Sd**.[10] Moreover, the desulfurization[12] of methylated **7Sd** with Raney nickel gave 6-methoxy-3,7-dimethyl-2-phenyl-4-chromanone (**10**, 42%) (Eq. 3).

Similarly, other alkylthioquinones **5Sd—f** reacted to afford **7Sb—f** in good yields together with minor products **8Sd—f** (Table 1). Product **8S** was independently prepared from **7S** by oxidation with chloranil or 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ).[10]

Thus, the photochemical reaction of alkylthioquinones **5S** in benzene solution was similar to that of alkoxyquinones **5G**. However, the photochemical reaction of **5Sb** was more effective than that of **5Gb**, as shown in Fig. 1.

Irradiation of 3-*t*-butylthio-5-methyl-2-(α-methylcinnamoyl)-1,4-benzoquinone (**5Sg**) for 3 h under the same conditions, however, gave no products and most of **5Sg** was recovered. Therefore, the present reaction proceeds via γ-hydrogen abstraction from the alkylthio group. As expected, the quantum yield of the disappearance of isopropylthioquinone (**5Sd**, Φ=0.50) is larger than that of ethylthioquinone (**5Sb**, Φ=0.30).

Photochemical Reaction of 11G and 11S. Irradiation of an acetonitrile solution of 2-cinnamoyl-3-methoxy-5-methyl-1,4-benzoquinone (**11Ga**), which has no α-methyl group in the alkenoyl side chain, afforded a mixture of 8-methyl-5-phenyl-5*H*-pyrano-[4,3,2-*de*][1,3]benzodioxin-9-ol (**13Ga**, 24%) and 2-cinnamoyl-3-methoxy-5-methylhydroquinone (**15Ga**, 7%) (Eq. 4). The products were separated by column chromatography after acetylation. The structure of each acetate was determined on the basis of spectral data (see Experimental). Other alkoxyquinones, **11Gb** and **11Gd**, similarly reacted to give a mixture of the corresponding **13G** and **15G**. In the case of the reaction of **11Gd** another minor product **14Gd** was obtained.



11G (X=O) 12G 13G 14G 15G

11S (X=S) 12S 13S 14S 15S

a: $R^1=R^2=H$; b: $R^1=H$, $R^2=Me$; d: $R^1=R^2=Me$ (4)

Irradiation of a benzene solution of 2-cinnamoyl-3-ethylthio-5-methyl-1,4-benzoquinone (**11Sb**) for 3 h gave a mixture of 2,8-dimethyl-5-phenyl-5*H*-pyrano-[4,3,2-*de*][3,1]benzoxathiin-9-ol (**13Sb**, 31%), 2,4-dimethyl-7-phenyl-9*H*-[1,3]oxathiolo[4,5-*f*][1]benzo-pyran-9-one (**14Sb**, 29%), and hydroquinone (**15Sb**, 12%). After separation by column chromatography their structures were determined on the basis of spectral data. Another quinone **11Sd** similarly reacted to give a mixture of **13Sd**, **14Sd**, and **15Sd**. The yields of the products are summarized in Table 2.

Effect of α-Methyl Group in the Alkenoyl Side Chain. As shown in Tables 1 and 2, the yields of **13** are appreciably less than those of **7**. Thus, the presence of the α-methyl group in the alkenoyl side chain is favorable for a higher yield of **7**. The structural change of alkyl groups in the alkoxyl or alkylthio groups in **11** only slightly affects the yield of product **13**. Therefore, the differences of the yields between **7** and **13** could be ascribed to the presence or absence of the α-methyl group in the alkenoyl side chain. These results may be explained on the basis of the equilibrium of intermediates **17** and **18** or **20** and **21**, as shown in Scheme 1. The ratio of **17**/**18** could be larger than that of **20**/**21** because of a steric hindrance of the methyl group derived from the alkenoyl side chain. This is one reason why the amount of product **7** is greater than that of **13**.

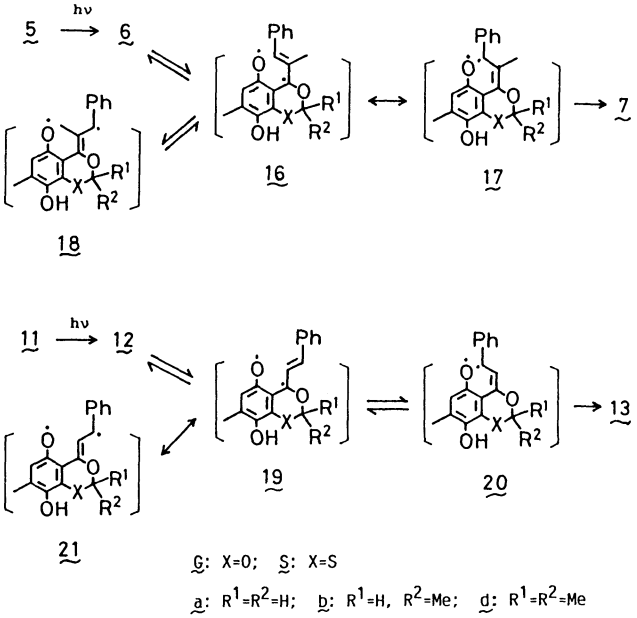
Table 2. Photochemical Reaction of **11**

Quinone	Substituents		Yields of products/%[a]		
	R^1	R^2	**13**	**14**	**15**
11Ga	H	H	24	0	7
11Gb	H	Me	30	0	16
11Gd	Me	Me	28	10	18
11Sb	H	Me	31	29	12
11Sd	Me	Me	58	19	9

a) Isolated yields based on the quinone used. The starting quinones **11Ga**, **b**, and **d** were recovered in 40, 37, and 15% yields, respectively, and **11S** was not recovered.

On the other hand, the hydrogen at the 5-position of products **7** and **13** should be highly activated, since its hydrogen is situated in the benzylic, allylic, and alkoxyl α-position. Actually, product **13** was easily oxidized by quinone **11** to give **14**.[10,13] Contrary to the expectation, the hydrogen at the 5-position of **7S** is resistant[14] to oxidation owing to the bigger steric hindrance from the surrounding methyl group. As a result, product **7** is moderately more stable than **13**.

Photochemical Reaction of 5 in Alcohols. Upon



G: X=O; S: X=S

a: $R^1=R^2=H$; b: $R^1=H$, $R^2=Me$; d: $R^1=R^2=Me$

Scheme 1.

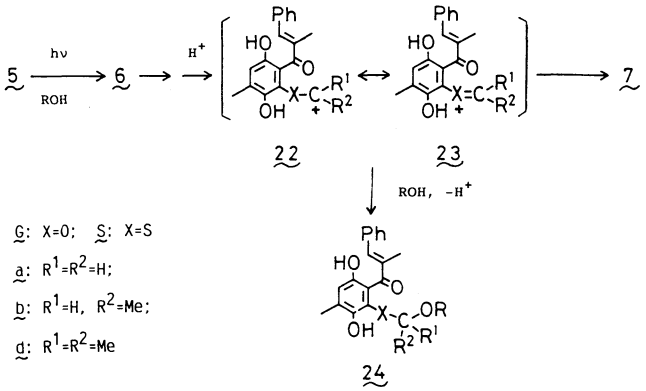
Table 3. Photochemical Reaction of **5** in Alcohols

Run	Quinone	Substituents		Solvent	Yields of products/%[a]			
		R^1	R^2		**7**	**8**	**24**	**5H**[b]
1	**5Ga**	H	H	MeOH	43	0	0	10
2	**5Gb**	H	Me	MeOH	32	0	5	21
3				*i*-PrOH	70	0	0	7
4	**5Gd**	Me	Me	MeOH	83	0	0	13
5	**5Sb**	H	Me	MeOH	22	0	50	10
6				EtOH	51	14	15	5
7				*i*-PrOH	82	6	5	3
8				*t*-BuOH	80	8	0	4
9	**5Sd**	Me	Me	MeOH	80	5	0	5

a) Isolated yields based on the quinone used. The other alcohol adducts (type **3** and **4**) and minor unidentified products were obtained. b) **5H** is the hydroquinone of **5**.

irradiation in a methanol solution, the quinones **5** reacted competitively to give cyclization products **7** and/or alcohol adducts (type **3** and **4**, see Eq. 1).[5] As shown in Table 3, all the quinones **5** gave cyclization products **7**. Especially, **5Gd** and **5Sd**, having an isopropoxy or isopropylthio group at the 3-position, gave cyclization products **7Gd** and **7Sd** in high yields (Runs 4 and 9). Thus, the γ-hydrogen abstraction was more preferential than the adduct formation with alcohol.[5]

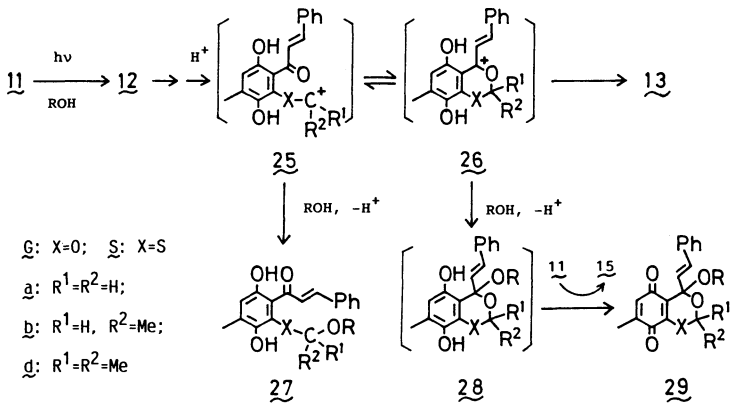
On the other hand, ethylthioquinone **5Sb** (Run 5) gave another type of methanol adduct **24SbM** (50%, R=Me). The adduct **24SbM** can be afforded by the addition of methanol to the cationic intermediate **22Sb**, which probably forms by an intramolecular electron transfer of **6Sb** followed by a protonation and is stabilized by conjugation with a lone-pair electron of the adjacent sulfur atom, as indicated in **23Sb** (Scheme 2). However, isopropylthioquinone **5Sd** (Run 9) gave no methanol adduct **24SdM**, though the cyclization product **7Sd** was obtained in high yield. This can be explained by a steric hindrance for the addition of methanol to the tertiary cation of intermediate **22Sd** (R^1=R^2=Me). The presence of such a steric hindrance can also be supported by the fact that the formation of the alcohol adduct **24Sb** decreased in turn from methanol to ethyl, isopropyl, and *t*-butyl alcohols (Runs 5—8) and the formation of the cyclization product **7Sb** was increased in this order.



Scheme 2.

In the case of ethoxyquinone **5Gb**, only a small amount of **24Gb** was isolated. It may be suggested that the intermediate **22Gb** is less reactive with alcohols than **22Sb**. On the other hand, since the reaction of **5Gb** in isopropyl alcohol (Run 3) gave **7Gb** in high yield, the absence of the adduct **24Gd** in the reaction of the isopropoxyquinone **5Gd** (Run 4) must also be ascribed to the same reason applied for the case of isopropylthioquinone **5Sd**.

Photochemical Reaction of 11 in Alcohols. The reaction of a methanol solution of **11S**, which has no α-methyl group in the alkenoyl side chain (Table 4, Runs 14 and 15), showed a similar tendency to that of **5S**: The quinones **11S** gave cyclization products **13S**



Scheme 3.

Table 4. Photochemical Reaction of **11** in Alcohols

Run	Quinone	Substituents		Solvent	Yields of products/%[a]			
		R^1	R^2		**13**	**27**	**29**	**15**
10	**11Ga**	H	H	MeOH	0	0	16	30
11				*i*-PrOH	9	0	6	16
12	**11Gb**	H	Me	MeOH	0	0	18	32
13	**11Gd**	Me	Me	MeOH	0	0	15	35
14	**11Sb**	H	Me	MeOH	22	22	0	23
15	**11Sd**	Me	Me	MeOH	84	0	0	6

a) Isolated yields based on the quinone used. The other alcohol adducts (type **3** and **4**), **14S**, and other minor products were obtained.

and/or methanol adducts (type **3** and **4**); especially **11Sd**, having an isopropylthio group, afforded **13Sd** in high yield. The ethylthioquinone **11Sb** also gave another methanol adduct **27SbM** (22%, R=Me).

In contrast, the irradiation of alkoxyquinones **11G** in methanol (Table 4, Runs 10, 12, and 13) gave no cyclization product **13G**; however, another methanol adduct **29GM** (R=Me) was obtained in considerable yield. Moreover, no other methanol adduct **27G** was formed.

The structure of **29G** was confirmed by its spectral data and by chemical derivations with zinc–acetic anhydride (see Experimental). As shown in Scheme 4, the adduct **29G** can be formed by the addition of an alcohol to cationic intermediate **26G**, followed by oxidation with the starting quinone **11G**. The reaction of **11Ga** in isopropyl alcohol (Run 11) gave not only the adduct **29GaP** (R=*i*-Pr) but also cyclization product **13Ga**, because the addition of an isopropyl alcohol to **26G** becomes difficult for the steric hindrance.

As described above, the product distribution of **11G** in methanol differed from that of **11S** (Table 4). These differences obviously reflect the relative stability of the cationic intermediates, **25G** and **25S**. Thus, the reaction in alcohols proceeds by an ionic process.

In conclusion, upon the irradiation of alkenoylquinones in acetonitrile or benzene, **5** and **11** readily afforded tricyclic compounds **7** and **13**, respectively. The reaction was initiated by the abstraction of γ-hydrogen; the resulting diradical intramolecularly cyclizes the involved alkenoyl side chain to give **7** or **13**. The presence of an α-methyl group in the alkenoyl side chain affects the yield as well as the stability of product **7**. Upon irradiation in alcohol, the reaction probably proceeds through an ionic process via the cationic intermediates to give the products.

Experimental

The instruments and procedures were as previously reported.[5] 3-Alkoxy-5-methyl-2-(α-methylcinnamoyl)-1,4-benzoquinones (**5G**) were prepared by a modified method of

Table 5. Yields and Physical Data of **5** and **11**

Quinone	Yield %	Mp θ_m/°C	IR(CCl_4) cm^{-1}	^1H NMR(CCl_4) δ(J/Hz)/ppm
5Ga	95	103—104	1670	2.02 (3H, s), 2.10 (3H, s), 3.88 (3H, s), 6.38 (1H, s), 7.12 (1H, s), 7.28 (5H, s).
5Gb	95	78—80	1670	1.26 (3H, t, J=7), 1.99 (3H, s), 2.07 (3H, s), 4.14 (2H, q, J=7), 6.38 (1H, s), 7.12 (1H, s), 7.8 (5H, s).
5Gc[a]	89	74—75	1670	0.89 (3H, t, J=7), 1.62 (2H, m, J=7), 1.98 (3H, s), 2.08 (3H, s), 4.05 (2H, t, J=7), 6.36 (1H, s), 7.19 (1H, s), 7.26 (5H, s).
5Gd	60	103—105	1670	1.21 (6H, d, J=6), 1.99 (3H, s), 2.07 (3H, s), 4.78 (1H, m, J=6), 6.38 (1H, s), 7.08 (1H, s), 7.27 (5H, s).
5Ge[a,b]	55	Oil	1670	0.86 (3H, t, J=7), 1.17 (3H, d, J=6), 1.3—1.8 (2H, m), 2.03 and 2.08 (6H, each s), 4.67 (1H, m, J=6), 6.41 (1H, s), 7.13 (1H, s), 7.31 (5H, s).
5Gf[a,b]	76	101—102	1665	2.01 and 2.07 (6H, each s), 5.23 (2H, s), 6.43 (1H, s), 7.14 (1H, s), 7.25 and 7.32 (10H, each s).
5Sb	88	90—92	1660	1.20 (3H, t, J=7), 2.04 and 2.09 (6H, each s), 2.93 (2H, q, J=7), 6.43 (1H, s), 7.05 (1H, s), 7.28 (5H, s).
5Sc	91	88—90	1665	0.93 (3H, t, J=7), 1.56 (2H, m, J=7), 2.06 and 2.12 (6H, each s), 2.93 (2H, t, J=7), 6.56 (1H, s), 7.18 (1H, s), 7.25—7.50 (5H, m).
5Sd	96	93—95	1660	1.23 (6H, d, J=7), 2.12 and 2.18 (6H, each s), 3.98 (1H, m, J=7), 6.63 (1H, s), 7.20 (1H, s), 7.40 (5H, s).
5Se	97	81—83	1665	0.93 (3H, t, J=7), 1.23 (3H, d, J=7), 1.51 (2H, m, J=7), 2.14 (3H, s), 2.22 (3H, s), 3.85 (1H, q, J=7), 6.69 (1H, s), 7.29 (1H, s), 7.47 (5H, s).
5Sf	83	Oil	1660	1.96 (3H, s), 2.08 (3H, s), 4.21 (2H, s), 6.41 (1H, s), 7.05 (1H, s), 7.12 (5H, s), 7.32 (5H, s).
5Sg	59	128—130	1670	1.37 (9H, s), 2.14 and 2.16 (6H, each s), 6.67 (1H, s), 7.08 (1H, s), 7.40 (5H, bs).
11Ga[c]	87	92—94	1660	2.12 (3H, s), 3.98 (3H, s), 6.57 (1H, bs), 6.92 (1H, d, J=16), 7.3—7.65 (6H, m).
11Gb[c]	85	139—141	1665	1.28 (3H, t, J=7), 2.06 (3H, s), 4.19 (2H, q, J=7), 6.52 (1H, bs), 6.86 (1H, d, J=16), 7.2—7.5 (6H, m).
11Gd	80	Oil	1670	1.21 (6H, d, J=6), 2.00 (3H, s), 4.84 (1H, m, J=6), 6.40 (1H, bs), 6.68 (1H, d, J=16), 7.1—7.6 (6H, m).
11Sb[c]	95	172—174	1655	1.20 (3H, t, J=7), 2.06 (3H, d, J=1.5), 2.96 (2H, q, J=7), 6.52 (1H, q, J=1.5), 6.80 (1H, d, J=17), 7.2—7.6 (6H, m).
11Sd[c]	90	170—172	1660	1.25 (6H, d, J=7), 2.15 (3H, s), 4.00 (1H, m, J=7), 6.69 (1H, s), 6.90 (1H, d, J=17), 7.3—7.7 (6H, m).

a) Reaction conditions: Benzene was used as solvent. b) Reaction conditions: 50 °C. c) $CDCl_3$ was employed for NMR solvent.

Farina and Valderrama[15] from 5-methyl-2-(α-methylcinnamoyl)-1,4-benzoquinone in the following manner. A mixture of 1 mmol of quinone, 1 mmol of $Cu(AcO)_2 \cdot H_2O$,[16] and 50 cm^3 of an alcohol (or added benzene for dissolving) was stirred at 40 °C in the dark overnight under an oxygen atmosphere. After removing the solvent, the residue was purified by column chromatography with benzene as the eluent. All of the obtained quinones **5G** were recrystallized from hexane containing a small amount of benzene to give yellow prisms. 3-Alkoxy-2-cinnamoyl-5-methyl-1,4-benzoquinones (**11G**) were also prepared in the same manner as for **5G** from 2-cinnamoyl-5-methyl-1,4-benzoquinone with the use of 5 mmol of AgOAc instead of $Cu(AcO)_2 \cdot H_2O$. Yields and physical data of **5G** and **11G** are summarized in Table 5.

2-Alkenoyl-3-alkylthio-1,4-benzoquinones, **5S** and **11S**, were also prepared in a similar manner, as follows. A mixture of 2-alkenoyl-1,4-benzoquinone (1 mmol) and thiol (2—10 mmol) in benzene (25 cm^3) was stirred at room temperature overnight under a nitrogen atmosphere. The obtained 2-alkenoyl-3-alkylthiohydroquinone was purified by column chromatography and oxidized with cerium(IV) ammonium nitrate (CAN, 2.5 equiv) at 5 °C for 5 min. The reaction mixture was worked up as usual. All of the resulting quinones were recrystallized from hexane containing a small amount of benzene as orange or reddish orange prisms. The yields and physical properties of quinones **5S** and **11S** are summarized in Table 5.

Photochemical Reaction of 5Ga—f. A solution of **5G** in acetonitrile (30 cm^3, 0.01 mol dm^{-3}) was irradiated with a 300-W halogen lamp through a yellow glass filter (Toshiba L-42; <410 nm cut off) under a nitrogen atmosphere for 3 h. After the solvent was removed under reduced pressure, the resulting oil was chromatographed on a column with benzene as the eluent. The first very pale-yellow eluate was **7G**, the second yellow eluate recovered was **5G**. The third was a mixture of unidentified products. In the cases of **5Gd** and **5Ge**, minor products **8Gd** and **8Ge** were obtained from the third eluate. The yields of the products are summarized in Table 1. Since products **7G** were not stable in air, IR and ^1H NMR data of **7G** are described for acetates which were prepared by the acetylation with acetic anhydride and pyridine. All of products **7G**, except **7Ga** and **d**, were a mixture of diastereoisomers. Only in the case of **7Gb**, could the diastereoisomers be separated into each isomer after acetylation by both recrystallization (from hexane containing small amounts of benzene) and TLC (benzene as developing solvent, Merk, Art. 5715).

9-Acetoxy-4,8-dimethyl-5-phenyl-5*H*-pyrano[4,3,2-*de*][1,3]-benzodioxin (acetate of **7Ga**): colorless prisms, mp 121—122.5 °C; IR ($CHCl_3$) 1760, 1705 (w), and 1195 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.50 (3H, s), 2.02 (3H, s), 2.26 (3H, s), 5.26 (1H, ABq, *J*=5 Hz), 5.31 (1H, ABq, *J*=5 Hz), 5.74 (1H, s), 6.17 (1H, s), 7.32 (5H, s). Found: C, 71.18; H, 5.64%. Calcd for $C_{20}H_{18}O_5$: C, 71.00; H, 5.36%.

9-Acetoxy-2,4,8-trimethyl-5-phenyl-5*H*-pyrano[4,3,2-*de*]-[1,3]benzodioxin (acetate of **7Gb**) (a mixture of diastereoisomers; ca. 3:1). Major diastereoisomer: oil; IR (CCl_4) 1770, 1705 (w), 1400, 1195 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ=1.50 (3H, s), 1.64 (3H, d, *J*=5.1 Hz), 2.07 (3H, s), 2.32 (3H, s), 5.34 (1H, q, *J*=5.1 Hz), 5.83 (1H, s), 6.21 (1H, s), 7.3—7.45 (5H, m). Minor diastereoisomer: colorless prisms; mp 150—152 °C; IR (CCl_4) 1770, 1700 (w), 1400, 1195 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ=1.55 (3H, s), 1.65 (3H, d, *J*=5.1 Hz), 2.05 (3H, s), 2.31 (3H, s), 5.25 (1H, q, *J*=5.1 Hz), 5.76 (1H, s), 6.19 (1H, s), 7.33 (5H, s). Found: C, 71.42; H, 5.69%. Calcd for $C_{21}H_{20}O_5$: C, 71.58; H, 5.72%.

9-Acetoxy-2-ethyl-4,8-dimethyl-5-phenyl-5*H*-pyrano[4,3,2-*de*][1,3]benzodioxin (acetate of **7Gc**) (a mixture of diastereoisomers; 1:1): oil; IR (CCl_4) 1765 and 1190 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ=1.08 (3H, t, *J*=7.6 Hz), 1.49 and 1.55 (3H, each s), 1.9—2.25 (2H, m), 2.05 and 2.06 (3H, each s), 2.30 (3H, s), 5.03 and 5.12 (1H, each d, *J*=5.3 Hz), 5.75 and 5.83 (1H, each s), 6.18 and 6.20 (1H, each s), 7.3—7.5 (5H, m). Found: *m/z* 366.1444. Calcd for $C_{22}H_{22}O_5$: M, 366.1465.

9-Acetoxy-2,2,4,8-tetramethyl-5-phenyl-5*H*-pyrano[4,3,2-*de*][1,3]benzodioxin (acetate of **7Gd**): colorless prisms, mp 154—155 °C; IR (CCl_4) 1765, 1645, 1190 cm^{-1}; ^1H NMR (CCl_4) δ=1.50, 1.56, and 1.60 (9H, each s), 2.01 (3H, s), 2.25 (3H, s), 5.73 (1H, s), 6.11 (1H, s), 7.32 (5H, s). Found: C, 72.04; H, 5.98%. Calcd for $C_{22}H_{22}O_5$: C, 72.11; H, 6.05%.

9-Acetoxy-2-ethyl-2,4,8-trimethyl-5-phenyl-5*H*-pyrano[4,3,2-*de*][1,3]benzodioxin (acetate of **7Ge**) (a mixture of diastereoisomers; 1:1): oil; IR (CCl_4) 1770, 1645, 1190 cm^{-1}; ^1H NMR (CCl_4) δ=0.98 and 1.01 (3H, each t, *J*=7 Hz), 1.49 and 1.52 (6H, each s), 1.65—2.05 (2H, m, *J*=7 Hz), 2.00 (3H, s), 2.18 (3H, s), 5.70 (1H, s), 6.08 (1H, s), 7.30 (5H, s). Found: *m/z* 380.1623. Calcd for $C_{23}H_{24}O_5$: M, 380.1623.

9-Acetoxy-4,8-dimethyl-2,5-diphenyl-5*H*-pyrano[4,3,2-*de*]-[1,3]benzodioxin (acetate of **7Gf**) (a mixture of diastereoisomers; 2:1): oil; IR (CCl_4) 1760, 1700 (w), 1365, 1190 cm^{-1}; ^1H NMR (CCl_4) δ=1.50 and 1.57 (3H, each s), 2.06 (3H, s), 2.20 (3H, s), 5.70 and 5.81 (1H, each s), 6.10 (1H, s), 6.16 and 6.20 (1H, each s), 7.2—7.7 (10H, m). Found: *m/z* 414.1472. Calcd for $C_{26}H_{22}O_5$: M, 414.1466.

2,2,4,8-Tetramethyl-7-phenyl-9*H*-[1,3]dioxolo[5,4-*f*][1]-benzopyran-9-one (**8Gd**): colorless solid, mp 172—174 °C; IR (CCl_4) 1640, 1460 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.79 (6H, s), 2.08 (3H, s), 2.28 (3H, s), 6.70 (1H, s), 7.4—7.65 (5H, m). Found: C, 74.66; H, 5.80%. Calcd for $C_{20}H_{18}O_4$: C, 74.52; H, 5.63%.

2-Ethyl-2,4,8-trimethyl-7-phenyl-9*H*-[1,3]dioxolo[5,4-*f*][1]-benzopyran-9-one (**8Ge**): oil; IR (CCl_4) 1635, 1460 cm^{-1}; ^1H NMR (CCl_4) δ=1.07 (3H, t, *J*=7 Hz), 1.70 (3H, s), 2.02 (3H, s), 2.03 (2H, q, *J*=7 Hz), 2.26 (3H, s), 6.61 (1H, s), 7.4—7.7 (5H, m).

Photochemical Reaction of 5Sb—f. A benzene solution of **5S** was irradiated for 1.5 h under the same conditions as for **5G**. After removing the solvent in vacuo, the residue was chromatographed on a column with benzene as the eluent. The first pale-yellow eluate was **7S** and the second yellow eluate was **8S**. The starting quinone **5S** was not recovered. Since products **7S** were unstable, they were methylated with methyl iodide and potassium carbonate in dry acetone in the usual way. In addition, unstable products **7S** were converted to stable **8S** by oxidation[10] and their elemental analyses were measured unless otherwise noted. The yields of products **7S** and **8S** are tabulated in Table 1. IR and ^1H NMR data of **7S** are described for methyl ether, and those of other **8S** were referred to in a preceding paper.[10]

9-Methoxy-2,4,8-trimethyl-5-phenyl-5*H*-pyrano[4,3,2-*de*]-[3,1]benzoxathiin (methyl ether of **7Sb**) (a mixture of diastereoisomers; 5:1): oil; IR (CCl_4) 1680 (w), 1470, and 1210 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.49 and 1.62 (3H, each s), 1.71 and 1.73 (3H, each, d, *J*=6 Hz), 2.11 and 2.14 (3H, each

s), 3.66 (3H, s), 4.90—5.25 (1H, m, J=6 Hz), 5.51 and 5.64 (1H, each s), 6.17 and 6.22 (1H, each s), 7.15—7.4 (5H, m). Found: m/z 340.1149. Calcd for $C_{20}H_{20}O_3S$: M, 340.1132.

2-Ethyl-9-methoxy-4,8-dimethyl-5-phenyl-5*H*-pyrano[4,3,2-*de*][3,1]benzoxathiin (methyl ether of **7Sc**) (a mixture of diastereoisomers; 3:1): oil; IR (CCl_4) 1675 (w), 1470, 1200 cm^{-1}; ^1H NMR (CCl_4): δ=1.15 (3H, t, J=7 Hz), 1.52 and 1.63 (3H, each s), 1.85—2.3 (2H, m), 2.12 and 2.16 (3H, each s), 3.69 (3H, s), 4.90 and 5.01 (1H, each t, J=6 Hz), 5.58 and 5.70 (1H, each s), 6.23 and 6.28 (1H, each s), 7.37 (5H, s).

9-Methoxy-2,2,4,8-tetramethyl-5-phenyl-5*H*-pyrano[4,3,2-*de*][3,1]benzoxathiin (methyl ether of **7Sd**): oil; IR (CCl_4) 1670 (w), 1470, 1210 cm^{-1}; ^1H NMR (CCl_4) δ=1.56, 1.65, and 1.74 (9H, each s), 2.10 (3H, s), 3.60 (3H, s), 5.57 (1H, s), 6.14 (1H, s), 7.22 (5H, s). Found: m/z 354.1285. Calcd for $C_{21}H_{22}O_3S$: M, 354.1289.

2-Ethyl-9-methoxy-2,4,8-trimethyl-5-phenyl-5*H*-pyrano[4,3,2-*de*][3,1]benzoxathiin (methyl ether of **7Se**) (a mixture of diastereoisomers; 1:1): oil; IR (CCl_4) 1670 (w), 1450, 1395 cm^{-1}; ^1H NMR δ=1.03 and 1.10 (3H, each t, J=7 Hz), 1.58, 1.60, and 1.68 (6H, each s), 1.8—2.4 (2H, m), 2.13 (3H, s), 3.66 (3H, s), 5.65 (1H, s), 6.22 (1H, s), 7.30 (5H, s).

9-Methoxy-4,8-dimethyl-2,5-diphenyl-5*H*-pyrano[4,3,2-*de*]-[3,1]benzoxathiin (methyl ether of **7Sf**) (a mixture of diastereoisomers; 7:3): oil; IR (CCl_4) 1675 (w), 1470, 1400, 1210 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ=1.55 and 1.68 (3H, each s), 2.16 and 2.20 (3H, each s), 3.76 (3H, s), 5.73 and 5.86 (1H, each s), 6.08 and 6.18 (1H, each s), 6.40 and 6.47 (1H, each s), 7.3—7.8 (10H, m).

2,2,4,8-Tetramethyl-7-phenyl-9*H*-[1,3]oxathiolo[4,5-*f*][1]-benzopyran-9-one (**8Sf**): orange prisms, mp 154—156 °C; IR ($CHCl_3$) 1620, 1430 cm^{-1}; ^1H NMR (CCl_4) δ=2.04 (3H, s), 2.32 (3H, s), 6.88 (1H, s), 7.07 (1H, s), 7.30—7.75 (10H, m). Found: C, 74.60; H, 4.77%. Calcd for $C_{24}H_{18}O_3S$: C, 74.59; H, 4.70%.

Photochemical Reaction of 11Ga—d. The procedures were same as described above for **5G**. The first yellow eluate was a mixture of cyclization product **13G** and hydroquinone **15G**. The yields of **13G** and **15G** were determined by ^1H NMR spectra and the isolation of those was carried out after acetylation in the usual manner. The second orange eluate was recovered **11G** and the third was a mixture of unidentified decomposition products. In the case of **11Gd**, minor product **14Gd** was contained in the third eluate. The yields of the products are summarized in Table 2. The structure of **15G** was identified by oxidation to **11G**.

9-Acetoxy-8-methyl-5-phenyl-5*H*-pyrano[4,3,2-*de*][1,3]-benzodioxin (acetate of **13Ga**): yellow oil; IR (CCl_4) 1765, 1190 cm^{-1}; ^1H NMR (CCl_4) δ=2.08 (3H, s), 2.24 (3H, s), 4.84 (1H, d, J=3.5 Hz), 5.28 (2H, s), 6.00 (1H, d, J=3.5 Hz), 6.21 (1H, s), 7.2—7.4 (5H, m). Found: m/z 324.1020. Calcd for $C_{19}H_{16}O_5$: M, 324.0996.

9-Acetoxy-2,8-dimethyl-5-phenyl-5*H*-pyrano[4,3,2-*de*][1,3]-benzodioxin (acetate of **13Gb**) (a mixture of diastereoisomers; 1:1): yellow oil; IR (CCl_4) 1765, 1190 cm^{-1}; ^1H NMR (CCl_4) δ=1.56 (3H, d, J=5 Hz), 2.01 and 2.04 (3H, each s), 2.20 and 2.25 (3H, each s), 4.72 and 4.78 (1H, each d, J=3 Hz), 5.18 (1H, q, J=5 Hz), 5.85—6.05 (1H, m), 6.14 and 6.18 (1H, each s), 7.1—7.5 (5H, m). Found: m/z 338.1161. Calcd for $C_{20}H_{18}O_5$: M, 338.1153.

9-Acetoxy-2,2,8-trimethyl-5-phenyl-5*H*-pyrano[4,3,2-*de*]-[1,3]benzodioxin (acetate of **13Gd**): yellow oil; IR (CCl_4) 1765, 1200 cm^{-1}; ^1H NMR (CCl_4) δ=1.55 (6H, s), 2.02 (3H, s), 2.18 (3H, s), 4.74 (1H, s, J=3 Hz), 5.95 (1H, d, J=3 Hz), 6.10 (1H, s), 7.1—7.4 (5H, m). Found: m/z 352.1293. Calcd for $C_{21}H_{20}O_5$: M, 352.1308.

2,2,4-Trimethyl-7-phenyl-9*H*-[1,3]dioxolo[5,4-*f*][1]benzopyran-9-one (**14Gd**): pale yellow prisms, mp 168—170 °C; IR (CCl_4) 1650, 1450 cm^{-1}; ^1H NMR (CCl_4) δ=1.74 (6H, s), 2.24 (3H, s), 6.40 (1H, s), 6.65 (1H, s), 7.3—7.5 (3H, m), 7.7—7.9 (2H, m). Found: m/z 308.1019. Calcd for $C_{19}H_{16}O_4$: M, 308.1047.

Photochemical Reaction of 11Sb and d. The procedures were the same as described above for **5S**, except the reaction time was 3 h. The first yellow eluate was a mixture of **13S** and **15S**; their yields were determined by ^1H NMR spectra; separation was achieved after methylation in the usual manner. The second yellow eluate was **14S** and the third was a mixture of unknown decomposition products. Products **13S** were more unstable than **7S**; therefore, elemental analyses of **13S** were achieved with **14S** after oxidation with chloranil. The results are summarized in Table 2. The IR and ^1H NMR data of **13S** are shown for the methyl ether.

9-Methoxy-2,8-dimethyl-5-phenyl-5*H*-pyrano[4,3,2-*de*][3,1]-benzoxathiin (methyl ether of **13Sb**) (a mixture of diastereoisomers; 1:1): oil; IR (CCl_4) 1660 (w), 1470, 1215 cm^{-1}; ^1H NMR (CCl_4) δ=1.65 and 1.67 (3H, each d, J=6 Hz), 2.10 and 2.14 (3H, each s), 3.60 and 3.62 (3H, each s), 4.8—5.1 (2H, m), 5.7—5.9 (1H, m), 6.20 and 6.29 (1H, each s), 7.1—7.4 (5H, m).

9-Methoxy-2,2,8-trimethyl-5-phenyl-5*H*-pyrano[4,3,2-*de*]-[3,1]benzoxathiin (methyl ether of **13Sd**): oil; IR (CCl_4) 1655 (w), 1470, 1210 cm^{-1}; ^1H NMR (CCl_4) δ=1.71 (6H, s), 2.18 (3H, s), 3.68 (3H, s), 5.09 (1H, d, J=4 Hz), 5.97 (1H, d, J=4 Hz), 6.37 (1H, s), 7.25—7.5 (5H, m).

2,4-Dimethyl-7-phenyl-9*H*-[3,1]oxathiolo[4,5-*f*][1]benzopyran-9-one (**14Sb**): yellow needles, mp 175—177 °C; IR ($CHCl_3$) 1630 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.77 (3H, d, J=6 Hz), 2.28 (3H, s), 6.21 (1H, q, J=6 Hz), 6.65 (1H, s), 6.94 (1H, s), 7.35—7.6 (3H, m), 7.7—7.95 (2H, m). Found: C, 69.46; H, 4.64%. Calcd for $C_{18}H_{14}O_3S$: C, 69.66; H, 4.55%.

2,2,4-Trimethyl-7-phenyl-9*H*-[3,1]oxathiolo[4,5-*f*][1]benzopyran-9-one (**14Sd**): yellow needles, mp 144—146 °C; IR (CCl_4) 1630 cm^{-1}; ^1H NMR (CCl_4) δ=1.85 (6H, s), 2.28 (3H, s), 6.60 (1H, s), 6.94 (1H, s), 7.4—7.6 (3H, m), 7.8—8.0 (2H, m). Found: C, 70.46; H, 5.01%. Calcd for $C_{19}H_{16}O_3S$: C, 70.35; H, 4.97%.

Photochemical Reaction of 5 in Alcohols. The procedures were the same as described above for **5G**, except regarding alcohol. In the reaction of **5Ga** in methanol, the first yellow eluate was a minor unidentified product; the second pale-yellow eluate was **7Ga** (43%); the third was a mixture of type **3** adduct (18%), type **4** adduct (7%), and **15Ga** (10%) which were separated by TLC with benzene as developing solvent after acetylation; and the fourth was a mixture of chromone derivative (3%) and chromamone derivative (8%) which were separated by TLC with chloroform as the developing solvent.

5-Acetoxy-4-methoxy-2-(α-methoxybenzyl)-2,6-dimethyl-benzofuran-3(2*H*)-one (acetate of type **3** adduct) (a mixture of diastereoisomers; 3:1): oil; IR (CCl_4) 1770, 1715, 1625, 1195 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.14 and 1.59 (3H, each s), 2.09, 2.19, 2.22, and 2.31 (6H, each s), 3.06 and 3.29 (3H, each s), 3.87 and 4.12 (3H, each s), 4.40 (1H, s), 6.65 and 6.71

(1H, each s), 7.1—7.5 (5H, m).

Methyl 3-acetoxy-2-methoxy-4-methyl-6-(α-methylstyryloxy)-benzoate (acetate of type **4** adduct) (a mixture of cis-trans isomers; 2:1): oil; IR (CCl_4) 1770, 1735, 1190 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.95, 2.08, 2.14, and 2.31 (6H, each s), 3.82 and 3.85 (6H, each s), 5.80 and 5.96 (1H, each s), 6.57 and 6.70 (1H, each s), 7.1—7.6 (5H, m).

6-Hydroxy-5-methoxy-2,7-dimethyl-3-phenyl-4*H*-1-benzopyran-4-one: solid; IR ($CHCl_3$) 3500, 1630 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.22 (3H, s), 2.38 (3H, s), 3.94 (3H, s), 6.09 (1H, s), 7.02 (1H, s), 7.2—7.5 (5H, m).

6-Hydroxy-2,5-dimethoxy-2,7-dimethyl-3-phenyl-4-chromanone (a mixture of diastereoisomers; 1:1): oil; IR ($CHCl_3$) 3525, 1690 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.36 and 1.39 (3H, each s), 2.26 and 2.30 (3H, each s), 3.18 and 3.22 (3H, each s), 3.75 and 3.84 (3H, each s), 3.65 and 4.03 (1H, each s), 5.76 (1H, bs), 6.60 and 6.67 (1H, each s), 7.22 and 7.31 (5H, each s).

Upon the reaction of **5Gb** and **d** in alcohols, the first yellow eluate was a minor unidentified product, the second pale yellow eluate was **7G**, the third was a mixture of hydroquinone containing the type **3** and **4** adducts, and the fourth was unknown products. In the case of **5Gb** the alcohol adduct **24GbM** (5%, R=Me) was isolated from the fourth eluate, even though in low yield. Since type **3** and **4** adducts yielded only a few per cent, most of them were not separated. The results are summarized in Table 3.

5-Acetoxy-4-ethoxy-2-(α-methoxybenzyl)-2,6-dimethylbenzofuran-3(2*H*)-one (acetate of type **3** adduct): oil; IR (CCl_4) 1770, 1715, 1625, 1195 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ=1.14 (3H, s) 1.37 (3H, t, *J*=7.1 Hz), 2.22 (3H, s), 2.34 (3H, s), 3.07 (3H, s), 4.03 (2H, dq-like, *J*=7.1 and 2.4 Hz), 4.41 (1H, s), 6.66 (1H, s), 7.35—7.55 (5H, m).

3-(1-Methoxyethoxy)-5-methyl-2-(α-methylcinnamoyl)-hydroquinone diacetate (diacetate of **24GbM**): oil; IR (CCl_4) 1770, 1625, 1365, 1185 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ=1.30 (3H, d, *J*=5.4 Hz), 2.14, 2.19, 2.22, and 2.34 (12H, each s), 3.28 (3H, s), 5.04 (1H, q, *J*=5.4 Hz), 6.85 (1H, s), 7.2—7.45 (6H, m).

Upon the reaction of **5S** in methanol, the first eluate was **7S**, the second was a minor unidentified prodcut, the third was **8S**, and fourth was a mixture of hydroquinone and **24S** which were separated as acetates after acetylation. However, in the case of **5Sd**, adducts **24Sd** were not isolated. The yields are summarized in Table 3.

Methyl 2-ethylthio-3-methoxy-4-methyl-6-(styryloxy)benzoate (methyl ether of type **4** adduct): oil; IR (CCl_4) 1740 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ=1.18 (3H, t, *J*=7.3 Hz), 2.30 (3H, s), 2.92 (2H, q, *J*=7.3 Hz), 3.84 (3H, s), 3.93 (3H, s), 6.32 (1H, d, *J*=12.4 Hz), 6.88 (1H, s), 7.03 (1H, d, *J*=12.4 Hz), 7.25—7.40 (5H, m).

3-(1-Methoxyethylthio)-5-methyl-2-(α-methylcinnamoyl)-hydroquinone diacetate (diacetate of **24SbM**: R=Me): colorless prisms, mp 96—97 °C; IR (CCl_4) 1770, 1655, 1365, and 1180 cm^{-1}; ^1H NMR (CCl_4) δ=1.39 (3H, d, *J*=6 Hz), 2.08, 2.15, 2.22, and 2.29 (12H, each s), 3.25 (3H, s), 4.68 (1H, q, *J*=6 Hz), 6.92 (1H, s), 7.01 (1H, s), 7.28 (5H, s). Found: C, 65.37; H, 6.00%. Calcd for $C_{24}H_{26}O_6S$: C, 65.14; H, 5.92%.

3-(1-Ethoxyethylthio)-5-methyl-2-(α-methylcinnamoyl)-hydroquinone diacetate (diacetate of **24SbE**: R=Et): colorless prisms, mp 97—99 °C; IR (CCl_4) 1775, 1660, 1370, and 1180 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ=11.4 (3H, t, *J*=7.1 Hz), 1.47 (3H, d, *J*=6.1 Hz), 2.14 (3H, s), 2.21 (3H, d, *J*=1.2 Hz), 2.24 (3H, d, *J*=0.5 Hz), 2.34 (3H, s), 3.30—3.45 (1H, m), 3.65—3.80 (1H, m), 4.89 (1H, q, *J*=6.1 Hz), 7.07 (1H, q, *J*=1.2 Hz), 7.09 (1H, q, *J*=0.5 Hz), 7.3—7.4 (5H, m).

3-(1-Isopropoxyethylthio)-5-methyl-2-(α-methylcinnamoyl)-hydroquinone (**24SbP**: R=*i*-Pr): oil; ^1H NMR (270 MHz, $CDCl_3$) δ=1.11 and 1.14 (6H, each d, *J*=6.1 Hz), 1.34 (1H, d, *J*=6.3 Hz), 2.24 (3H, s), 2.30 (3H, s), 3.79 (1H, m, *J*=6.1 Hz), 4.74 (1H, q, *J*=6.3 Hz), 6.66 (1H, bs), 6.81 (1H, s), 6.93 (1H, s), 7.30—7.45 (5H, m), 7.69 (1H, s).

Photochemical Reaction of 11 in Alcohols. The procedures were the same as described above for **5** in alcohol. Upon the reaction of **11G** in methanol, the first yellow eluate was a minor unidentified product, the second was **15G**, the third was **29GM** (R=Me), and the fourth was a mixture of methanol adducts (type **3** and **4**) and the starting quinone. Upon the reaction of **11Ga** in isopropyl alcohol, a mixture of **13Ga**, **29GaP** (R=*i*-Pr), and alcohol adducts (type **3** and **4**) was obtained from the third yellow eluate. The yields of the products were determined by ^1H NMR spectra and the isolation of those was carried out in the usual way after acetylation. The yields of the major products are summarized in Table 4.

4-Methoxy-7-methyl-4-styryl-4*H*-1,3-benzodioxin-5,8-dione (**29GaM**): oil; IR (CCl_4) 1680, 1660, 1610 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ=2.03 (3H, d, *J*=1.5 Hz), 3.34 (3H, s), 5.41 (1H, d, *J*=5.4 Hz), 5.50 (1H, d, *J*=5.4 Hz), 6.48 (1H, q, *J*=1.5 Hz), 6.71 (1H, d, *J*=16.1 Hz), 7.00 (1H, d, *J*=16.1 Hz), 72.5—7.40 (3H, m), 7.40—7.45 (2H, m); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=15.2 (q), 49.7 (q), 85.8 (t), 95.6 (s), 121.0 (s), 124.9 (d), 127.1 (d), 128.5 (d), 128.7 (d), 134.0 (d), 134.3 (d), 135.8 (s), 142.6 (s), 151.9 (s), 181.5 (s), 183.9 (s). Found: *m/z* 312.1009. Calcd for $C_{18}H_{16}O_5$: M, 312.0996.

4-Isopropoxy-7-methyl-4-styryl-4*H*-1,3-benzodioxin-5,8-dione (**29GaP**): oil; ^1H NMR (270 MHz, $CDCl_3$) δ=1.18 and 1.26 (6H, each d, *J*=6.1 Hz), 2.01 (3H, d, *J*=1.5 Hz), 4.23 (1H, m, *J*=6.1 Hz), 5.48 and 5.51 (2H, ABq, *J*=5.4 Hz), 6.45 (1H, q, *J*=1.5 Hz), 6.81 (1H, d, *J*=16.1 Hz), 7.01 (1H, d, *J*=16.1 Hz), 7.25—7.45 (5H, m).

4-Methoxy-2,7-dimethyl-4-styryl-4*H*-1,3-benzodioxin-5,8-dione (**29GbM**): oil; IR (CCl_4) 1680, 1660, 1610 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ=1.75 (3H, d, *J*=5.4 Hz), 2.02 (3H, d, *J*=1.5 Hz), 3.32 (3H, s), 5.52 (1H, q, *J*=5.4 Hz), 6.47 (1H, q, *J*=1.5 Hz), 6.71 (1H, d, *J*=16.1 Hz), 6.97 (1H, d, *J*=16.1 Hz), 7.25—7.45 (5H, m). Found: *m/z* 326.1151. Calcd for $C_{19}H_{18}O_5$: M, 326.1153.

4-Methoxy-2,2,7-trimethyl-4-styryl-4*H*-1,3-benzodioxin-5,8-dione (**29GdM**): oil; ^1H NMR (270 MHz, $CDCl_3$) δ=1.73 (3H, s), 1.81 (3H, s), 2.01 (3H, d, *J*=1.5 Hz), 3.35 (3H, s), 6.47 (1H, q, *J*=1.5 Hz), 6.62 (1H, d, *J*=16.1 Hz), 6.87 (1H, d, *J*=16.1 Hz), 7.25—7.45 (5H, m).

Upon the reaction of **11S** in methanol, the first eluate was type **4** adduct, the second was **13S**, the third was **15S**, and the fourth was a mixture of **14S** and **27S**. However, in the case of **11Sd**, the adducts **27Sd** was not isolated. The yields are summarized in Table 4.

2-Cinnamoyl-3-(1-methoxyethylthio)-5-methylhydroquinone diacetate (diacetate of **27SbM**: R=Me): colorless prisms, mp 127—129 °C; IR (CCl_4) 1770, 1650, 1175 cm^{-1}; ^1H NMR (CCl_4) δ=1.39 (3H, d, *J*=6 Hz), 2.09 (3H, s), 2.24 (3H, s), 2.32 (3H, s), 3.24 (3H, s), 4.67 (1H, q, *J*=6 Hz), 6.80 (1H, d, *J*=16 Hz), 7.02 (1H, s), 7.10 (1H, d, *J*=16 Hz), 7.15—7.6 (5H, m). Found: *m/z* 428.1280. Calcd for $C_{23}H_{24}O_6S$: M, 428.1291.

Reaction of 7Sd in the Presence of Chloroacetic Acid. A benzene solution (5 cm^3) of **7Sd** (0.15 mmol) and chloroacetic acid (ca. 0.5 mmol) in a sealed test tube was stirred at 40 °C for 2 days in the dark. The mixture was chromatographed on silica gel with benzene as the eluent. 2,2,4,8-Tetramethyl-7-phenyl-7,8-dihydro-9*H*-[1,3]oxathiolo[4,5-*f*][1]benzopyran-9-one (**9**, 63%) was obtained from the first yellow eluate. **9** (a mixture of diastereoisomers, ca. 9:2): yellow oil; IR (CCl_4) 2980, 1680, 1620, 1420 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ=0.98 and 1.00 (3H, each d, J=7.3 and 6.8 Hz), 1.83 (6H, s), 2.20 and 2.23 (3H, each s), 2.80 and 2.96 (1H, each dq, J=7.3 and 2.7 Hz and 12.2 and 6.8 Hz), 4.95 and 5.49 (1H, each d, J=12.2 and 2.7 Hz), 6.46 and 6.58 (1H, each s), 7.40 and 7.42 (5H, each s). Found: *m/z* 340.1112. Calcd for $C_{20}H_{20}O_3S$: M, 340.1132.

Desulfurization of Methylated 7Sd by Raney Nickel. A solution of methylated **7Sd** (0.22 mmol) in 95% ethanol (3 cm^3) was refluxed for 2 h with Raney nickel (ca. 0.5 g). The mixture was filtered, evaporated in vacuo, and the residue was chromatographed on silica gel with benzene as the eluent. 6-Methoxy-3,7-dimethyl-2-phenyl-4-chromanone (**10**, 42%) was obtained as major product from the second eluate. **10**: oil; IR (CCl_4) 1690, 1620, 1470, 1420, 1215 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ=0.98 (3H, d, J=7.3 Hz), 2.27 (3H, s), 2.77 (1H, dq, J=7.3 and 2.9 Hz), 3.85 (3H, s), 5.52 (1H, d, J=2.9 Hz), 6.92 (1H, s), 7.28 (1H, s), 7.35—7.5 (5H, m). Found: *m/z* 282.1243. Calcd for $C_{18}H_{18}O_3$: M, 282.1254.

Reductive Acetylation of 29GaM with Zinc-Acetic Anhydride. A mixture of **29GaM** (20 mg) and zinc dust (200 mg) in acetic anhydride (2 cm^3) containing two drops of pyridine was stirred at room temperature for 2 h. After removing the zinc, the reaction mixture was worked up in a similar manner to the usual acetylation. The residue was chromatographed on TLC with chloroform as the developing solvent. The first-moved band gave 5,8-diacetoxy-4-methoxy-7-methyl-4-styryl-4*H*-1,3-benzodioxin (diacetate of **28GaM**): 50%; colorless oil; IR (CCl_4) 1770, 1180 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ=2.17 (3H, d, J=0.5 Hz), 2.27 (3H, s), 2.34 (3H, s), 3.29 (3H, s), 5.26 and 5.29 (2H, ABq, J=5.6 Hz), 6.54 (1H, d, J=15.9 Hz), 6.60 (1H, bd, J=0.5 Hz), 6.87 (1H, d, J=15.9 Hz), 7.25—7.45 (5H, m). Found: *m/z* 398.1395. Calcd for $C_{22}H_{22}O_7$: M, 398.1365.

Quantum Yield Measurement. The quantum yield for consumed quinone **5Sd** was measured by potassium trioxalatoferrate(III) actinometry. A benzene solution of **5Sd** (0.5 mmol dm^{-3}) and a potassium trioxalatoferrate(III) solution (0.15 mol dm^{-3}) were employed. Conversion of the quinone (5—10%) was detected by UV spectrometer and the quantum yield of the disappearance of **5Sd** (Φ=0.50) was calculated in the usual way. The quantum yield of the disappearance of **5Sb** (Φ=0.30) was determined by a comparison with that of **5Sd**.

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14) By the treatment of **7Sd** with **5Sd** in the dark at 35 °C for 14 h, **7Sd** was recovered in a 71% yield. Even by the treatment of **7Sd** with chloranil in the dark at 35 °C for 3 h, **7Sd** was recovered in a 40% yield.

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