Dimethyldioxirane Epoxidation of Benzofurans: Reversible Thermal and Photochemical Valence Isomerization between Benzofuran Epoxides, Quinone Methides, and Benzoxetenes

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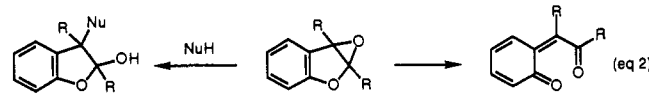
Abstract: Low-temperature oxidation of the four possible regioisomeric methoxy-substituted benzofurans **1** by dimethyldioxirane afforded the rather labile epoxides **2**, which are in equilibrium with their equally labile quinone methides **3** through reversible valence isomerization. Photochemical cyclization of the latter afforded the hitherto unknown benzoxetenes **4**, which are sufficiently persistent at subambient temperatures to permit spectral characterization. The labile oxetenes **4** slowly revert to the same equilibrium mixtures of the epoxides **2** and quinone methides **3** as are obtained in the dioxirane epoxidation of the benzofurans **1**. The mutual transformations of the benzofuran epoxides **2**, quinone methides **3**, and benzoxetenes **4** include thermal isomerization to the allylic alcohols **5** and their ring-opened tautomers **5′**, nucleophilic trapping in the form of the methanol adducts **6** and their ring-opened tautomers **6′**, inverse Diels–Alder reaction to the [4 + 2] cycloadducts **7**, and the 1,3-dipolar cycloaddition products **8** with tetracyanoethylene (TCNE).

The oxidation of furans is of current relevance and significance from the point of view of chemical[1] and toxicological[2] interest. On the one hand, the parent furan epoxide, the primary oxidation product, constitutes a highly reactive intermediate, which is held responsible for DNA damage through alkylation.[3] On the other hand, the strongly electrophilic *cis*-enedione, the valence isomer of the furan epoxide, has been shown to be cytotoxic and even mutagenic.[4] Thus, both the furan epoxides and *cis*-enediones play an important role as potentially malignant metabolites during enzymatic oxidation of furans in cellular systems.

To date no sufficiently persistent furan epoxides appear to be known even for spectral detection at subambient temperatures.[5] Presumably these putative intermediates valence-isomerize to the *cis*-enediones (eq 1) even below −80 °C and, thus, escape

(eq 1)

detection and isolation. However, we have demonstrated[6] that the related benzofuran epoxides, prepared either by dioxirane epoxidation of the benzofurans or by sulfide deoxygenation of the corresponding dioxetane,[2b,6d] are isolable at subambient temperatures. The fact that these epoxides are only persistent at low temperatures derives from their high reactivity, either through valence isomerization[6c] to the labile quinone methides or by efficient alkylation of nucleophiles (eq 2), quite analogous



(eq 2)

to their furan congeners (eq 1). It is, therefore, not surprising that benzofuran epoxides exhibit significant mutagenicity in the *Salmonella typhymurium* strain TA100.[7]

Recently[6c] we demonstrated for the epoxide of 2-methyl-3-phenylbenzofuran that the isomerization in eq 2 is reversible; in fact, the epoxide and its quinone methide appear to be in equilibrium with one another, as evidenced by the common chemistry exhibited by these labile valence isomers.

Presently we report on the dimethyldioxirane epoxidation of the methoxy-substituted 2,3-dimethylbenzofurans **1** to their labile epoxides **2** and the reversible isomerization of the latter to the quinone methides **3**, as revealed by the common chemistry shown in Scheme I. In addition we show that on irradiation of mixtures of **2** and **3** with visible light the hitherto unknown[8] benzoxetenes **4** were formed quantitatively. On warming, the novel benzoxetenes **4** revert to the same mixture of epoxides **2** and quinone

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Scheme I

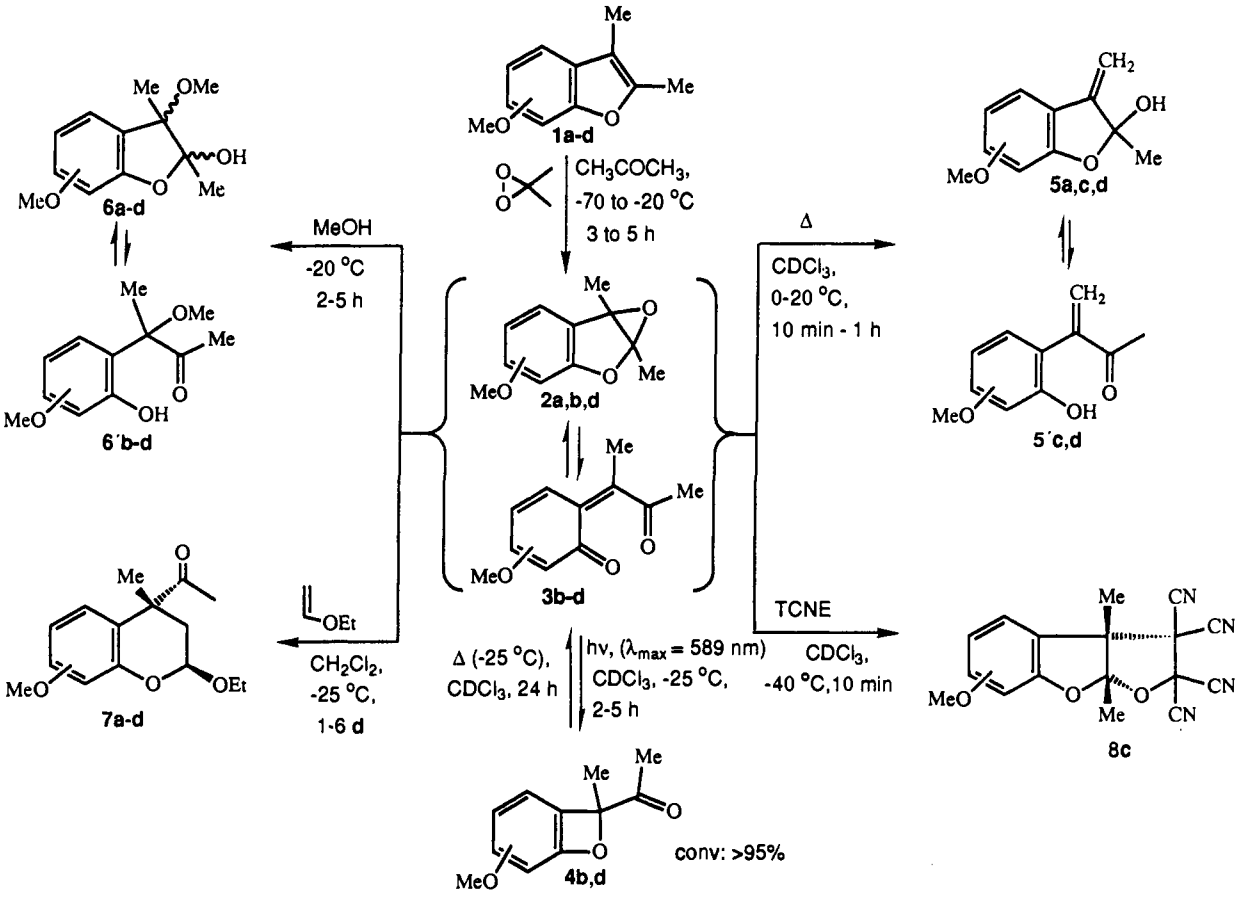


Table I: Product Studies[a] of the Dimethyldioxirane[b] Epoxidation[c] of Benzofurans **1** and Photolysis[d] of the Resulting Reaction Mixture

benzofuran **1**	epoxide **2**	quinone methide **3**	benzoxetene **4**
1a (4-OMe)	100	0	0[e]
1b (5-OMe)	34	66	>95
1c (6-OMe)	0	100	0[e]
1d (7-OMe)	57	43	>95

[a] Established by NMR integration, ca. 5% error of stated values. [b] Dioxirane as acetone solution (ca. 0.1 m). [c] Run at −70 to −20 °C for 2–4 h. [d] Na lamp (λ_{max} = 589 nm) run at −30 °C, 2–6 h. [e] Epoxide **2a** and quinone methide **3c** gave a complex product mixture on irradiation, which could not be characterized by ^{1}H and ^{13}C NMR.

methides **3** as obtained in the dioxirane oxidation of the benzofurans **1**. This observation provides for the first time unequivocal experimental proof that the epoxides **2** and quinone methides **3** are indeed in equilibrium with one another.

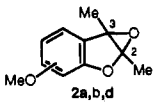
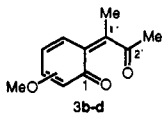
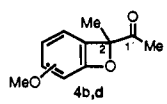
Results and Discussion

The epoxidation of the methoxy-substituted benzofurans **1** (Table I) was performed with isolated dimethyldioxirane (ca. 0.1 M) in acetone[9] by starting at −70 °C and warming up to −20 °C over a period of 2–4 h. The 4-methoxy derivative **1a** gave exclusively epoxide **2a**, while the 6-methoxy regioisomer **1c** led exclusively to the quinone methide **3c**, as confirmed by low-temperature ^{1}H and ^{13}C NMR. Selected ^{13}C NMR spectral data are given in Table II. The 5- and 7-methoxy cases **1b,d** afforded mixtures of **2b/3b** and **2d/3d** in proportions of 34:66 and 57:43, respectively (Table I).

The epoxides **2b,d** and quinone methides **3b,d** are produced in nearly equal amounts. Since these two valence isomers are in equilibrium with one another (Scheme I), this suggests that **2b,d** and **3b,d** are essentially isoenergetic; however, AM1 calculations reveal the contrary.[10]

Steric repulsion between the 4-methoxy substituent and the methyl group of the methide functionality in the quinone methide **3a** appears to be responsible for the exclusive formation of the epoxide isomer **2a** (eq 3). The valence isomerization of the parent benzofuran epoxide (also for the 5- and 7-methoxy derivatives **2b,d**) affords, as evidenced by the spectral data, the *Z* isomer[11]

Table II: Selected ^{13}C NMR Data[a] for the Valence Isomers **2–4**

valence isomer	nucleus	a	b	c	d
 **2a,b,d**	C-2	94.7	95.7		94.7
	C-3	66.9	67.0	b)	66.7
	2-Me	14.0	14.0		13.8
	3-Me	13.9	11.8		11.9
 **3b-d**	C-1		184.9	184.2	179.7
	C-1'		128.4	126.8	129.3
	C-2'	b)	206.6	206.7	206.6
	1'-Me		17.1	17.2	17.6
	2'-Me		26.9	26.9	26.3
 **4b,d**	C-2		100.9		102.8
	C-1'		205.2		205.5
	2-Me	b)	20.1	b)	20.1
	1'-Me		24.4		24.3

[a] For conditions see Experimental Section. [b] Was not detected.

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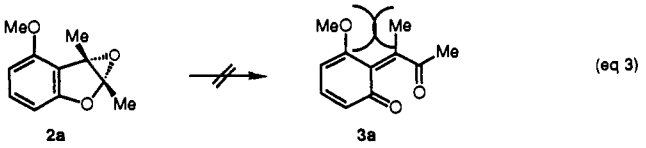
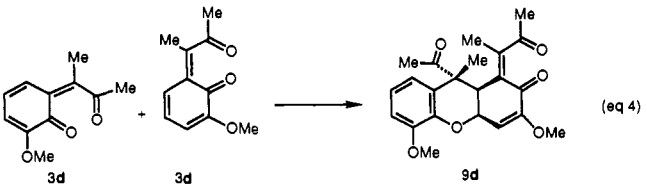
(10) Attempts were made to assess the electronic factors by AM1 computations, but for all methoxy regioisomers the quinone methides **3** were by ca. 20 kcal/mol lower in energy than the corresponding epoxides **2**. Thus, at this rudimentary semiempirical MO level the lack of aromaticity in the quinone methides **3** is more than compensated for by the composite effects of the loss of epoxide strain and gain of the two strong carbonyl double bonds.



2a 3a (eq 3)

with a planar arrangement of the methide substituent and the cyclohexadienone moiety for optimized conjugation. The 4-methoxy group prevents such planarity in **3a** through *peri* repulsion, and ring-opening does not occur.

Electronic reasons seem to operate in controlling the prevelence of quinone methide **3c**, but their nature is not at all obvious.[10] We speculate that since the 6-methoxy substituent in epoxide **2c** is *para* to the benzylic center, this should facilitate heterolysis of the epoxide ring by stabilization of the benzylic cation center and thereby promote valence isomerization to the quinone methide **3c**. The 5- and 7-methoxy regioisomers **2b,d** do not possess such an electronic driving force because the electron-donating substituents are in the *meta* position to the benzylic center, and mixtures of epoxides and quinone methides are obtained (Table I). Irrespective of whether one commences with the epoxide, e.g. **2a**, the quinone methide, e.g. **3c**, or the mixture of both, as in **2d** + **3d**, on warmup to room temperature (ca. 20 °C), within 1 h a mixture of the respective allylic alcohols **5a,c,d** and their ring-opened tautomers **5'c,d** was produced essentially quantitatively (Scheme I). However, on slow warmup of **2d**/**3d** (from −30 to 20 °C for 12 h), the dimer **9d** was obtained (eq 4), whose structure



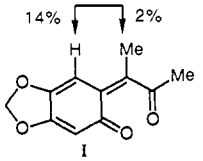
3d 3d 9d (eq 4)

was assigned by NOE experiments and whose HH and CH correlations were assigned by NMR spectroscopy. Only under these carefully controlled conditions could the [4 + 2]-type dimerization of **3d** be observed; much below −30 °C **3d** persisted, while fast warmup to room temperature led to a mixture of **5d** and **5'd**. The thermal behavior of **2b** + **3b** was problematic in that it afforded on warmup a complex mixture, in which several dimers **9b** were detected, but these were too labile even at room temperature for isolation and spectral characterization. Thus, only the 7-methoxy-substituted quinone methide **3d** dimerizes into a persistent cycloadduct **9d**.

The formation of the allylic alcohols **5a,c,d** may derive from transposition of a proton in the 1,3 dipole of the ring-opened epoxide **2** (Scheme II). The alternative that the *Z* isomer of the quinone methide **3** isomerizes to the *E* isomer under these conditions and the latter through 1,5 H shift affords **5'**, the ring-opened tautomers of **5**, is unlikely because in none of our examples have we observed *E* isomers of the quinone methides **3**. Also the strict retention of stereochemistry speaks against (*Z*)-**3** to (*E*)-**3** isomerization.

In the presence of methanol, already at −20 °C, within 2–5 h mixtures of the trapping products **6a–d** and their ring-opened tautomers **6'b–d** were observed in 52–87% yields (Scheme I).

(11) NOE experiments of I as a model compound confirmed the *Z* configuration of the quinone methides **3**. The acetyl and the olefinic methyl groups were assigned by CH correlation experiments.



I

This confirms once again the high alkylation propensity of these reactive epoxides in that while arene oxides[12] require base or acid catalysis for nucleophilic reactions, even at low temperatures benzofuran epoxides **2** do not. The driving force for the latter is aromatization during the Michael-type addition of nucleophiles to the intermediary quinone methides **3**, produced through the valence isomerization **2** ⇌ **3**. The resulting adducts **6'** cyclize in turn to their hemiacetals **6**.

Remarkable is the dimerization of epoxide **2d** and quinone methide **3d** to the [4 + 2] cycloadduct **9d**, when a mixture of **2d** and **3d** was allowed to warm up slowly to room temperature (eq 4). Since therewith the ability of the present quinone methides **3** to undergo [4 + 2] cycloaddition was manifested,[6c,13] the epoxides **2** and/or quinone methides **3** were treated with ethyl vinyl ether in CH_2Cl_2 at −30 °C for several days and the Diels–Alder adducts **7a–d** were obtained in 72–92% yields. As already stated before, the initial *Z* stereochemistry of the quinone methides **3** is strictly conserved in the benzopyran products **7**, as confirmed by the NMR data and NOE experiments.

With tetracyanoethylene (TCNE), quinone methide **3c** gave in $CDCl_3$ at −40 °C within 10 min the furofuran **8c** in 45% yield, whose structure was rigorously established by X-ray diffraction (Figure 1).[14] The epoxides **2a,b,d** and quinone methides **3b,d** yielded on reaction with TCNE complex mixtures, which contained furofuran products **8**, but which could not be purified by column chromatography or crystallization. The mechanism of furofuran **8c** formation is unclear at this stage because TCNE trapping of the 1,3 dipole (ring-opened epoxide **3c** in Scheme II) is unlikely in view of the expected short lifetime of such an intermediate.

The transformations in Scheme I convincingly demonstrate that a reversible valence isomerization operates between epoxide **2** and quinone methide **3**, in analogy to the 3-phenyl-2-methyl derivatives reported previously.[6c] How could epoxide **2a** produce the [4 + 2] cycloadduct **7a**, and quinone methide **3c** afford the allylic alcohol **5c**, were it not for the respective sequences **2a** → **3a** → **7a** and **3c** → **2c** → **5c**? The question, however, is whether these labile valence isomers coexist in equilibrium with one another. Definitive proof for this was provided by independent entry from the valence-isomeric benzoxetenes **4** (Scheme I). Irradiation of the mixtures **2b,d** + **3b,d** in $CDCl_3$ at 589 nm (sodium lamp) at −25 °C for 2–5 h generated quantitatively the corresponding oxetenes **4b,d**. The epoxide **2a** and quinone methide **3c** gave complex product mixtures on irradiation at 589 nm, which could not be characterized.

On standing at −25 °C, within 24 h the oxetenes **4b,d** regenerated the mixture of epoxides **2b,d** and quinone methides **3b,d** in the same proportion as was obtained in the dioxirane oxidation of the benzofurans **1b,d** (Table I). At ca. 20 °C the oxetene **4d** afforded the respective mixture of allylic alcohols **5d** and **5'd**. Furthermore, in the presence of ethyl vinyl ether the [4 + 2] cycloadducts **7b,d** were produced quantitatively. These events unequivocally establish that epoxides **2** and quinone methides **3** are in equilibrium with one another; thereby, all the mutual chemistry displayed in Scheme I can be accounted for. A related but irreversible valence isomerization was reported[15]

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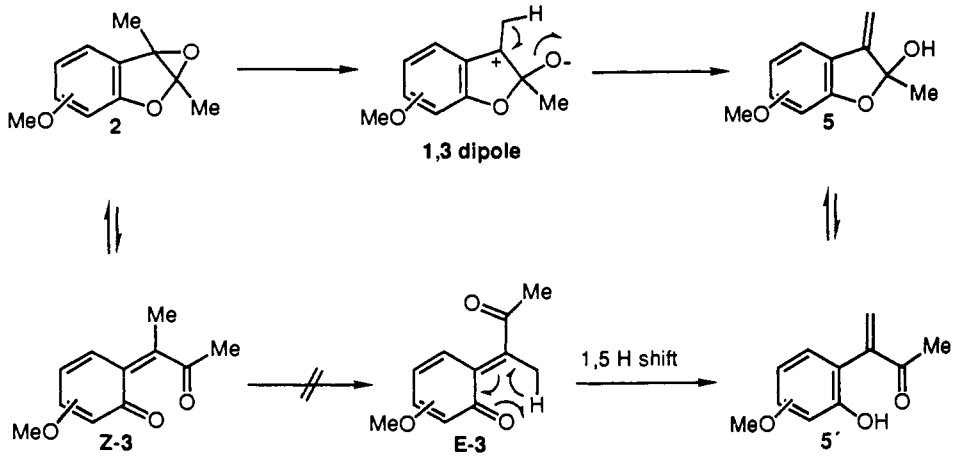
(13) Desimoni, G.; Tacconi, G. *Chem. Rev.* **1975**, *75*, 651–692.

(14) Furofuran **8d** (ether, mp 142–143 °C) is monoclinic and possesses the structural parameters $P2_1/c$, a = 981.0(4) pm, b = 1988.1(9) pm, c = 792.3(3) pm; β = 93.43(3)°; V = 1542(1) × 10^6 pm^3; Z = 4; d_{calc} = 1.380 g/cm^3; independent reflections, 3175 with $F > 3\sigma(F)$; R = 0.049, R_w = 0.044. Further details of the crystal structure for furofuran **8d** are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für Wissenschaftlich-Technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, Germany, by quoting the depository number (CSD-56761), the names of the authors, and the journal citation.

(15) Padwa, A.; Au, A.; Lee, G. A.; Owens, W. *J. Am. Chem. Soc.* **1976**, *98*, 3555–3564.

Scheme II



in the photolysis of 3-chromanones to oxabenzobicyclo[3.1.0]-hexenes through *o*-quinone allide and cyclopropanone intermediates.

In summary, not only has the oxidation of the four possible regioisomeric methoxy-substituted benzofurans **1** by dimethyldioxirane made possible the preparation of the rather labile benzofuran epoxides **2** but also their facile valence isomerization to the quinone methides **3** has opened the way for the synthesis of the hitherto unknown[8] benzoxetenes **4** through photocyclization. These novel, highly strained [2 + 2] cycloadducts readily revert thermally to an equilibrating mixture of quinone methides **3** and epoxides **2**, which are subject to a variety of mutual chemical transformations such as thermal isomerization to the allylic alcohols **5**, nucleophilic trapping to the methanol adducts **6**, inverse Diels–Alder reaction with ethyl vinyl ether to the [4 + 2] cycloadducts **7**, and the 1,3 dipolar cycloadducts **8** with TCNE.

Experimental Section

Melting points were determined on a Reichert Thermovar hot stage apparatus. The IR spectra were recorded on a Perkin-Elmer 1420 instrument. ^1H and ^{13}C NMR spectra were run on a Bruker AC 200 (200 MHz), AC 250 (250 MHz), or WM 400 (400 MHz) spectrometer. Chemical shifts refer to chloroform-*d*, methylene chloride-d_2, or acetone-d_6. Mass spectra were obtained on a Varian 8200 Finnigan Mat. Elemental analyses were performed in the Analytical Division of the Institute of Inorganic Chemistry (University of Würzburg). All solvents were purified by following standard literature methods. Dimethyldioxirane (as acetone solution) was prepared according to the published procedure;[9] its peroxide content was determined by oxidation of methyl phenyl sulfide to its sulfoxide, the latter quantitated by ^1H NMR. The dimethyldioxirane solutions were stored over molecular sieves at –20 °C.

2,3-Dimethylbenzo[*b*]furans **1a–e** were prepared in moderate overall yields according to literature procedures[16] by H_2SO_4 cyclization of 2-(aroyloxy)-1-alkyl-1-propanone, which in turn was obtained by the reaction of substituted phenols with 3-chloro-2-butanone in boiling butanone in the presence of K_2CO_3.

General Procedure for Epoxidation of 2,3-Dimethylbenzofurans 1a–d by Dimethyldioxirane. A cooled (–78 °C) solution of dimethyldioxirane (40–100% molar excess) in acetone (0.050–0.084 M), dried over molecular sieves at –20 °C, was rapidly added to a cooled (–78 °C), stirred solution of the 2,3-dimethylbenzofuran **1a–d** (0.84–1.00 mmol) in absolute CH_2Cl_2 (2 mL), under a N_2 atmosphere. The stirring was continued until complete consumption of the benzo[*b*]furan **1** (monitored by TLC), while the reaction temperature was allowed to increase to –20 °C. The solvent was evaporated (–20 °C at 0.01 Torr, 1–2 h) to yield quantitatively the hitherto unknown epoxides **2** or quinone methides **3** in high purity (^1H NMR), which deteriorated rapidly on standing at 0 °C.

2,3-Dihydro-2,3-dimethyl-2,3-epoxy-4-methoxybenzofuran (2a) was obtained quantitatively by following the above procedure at –78 to –20 °C for 2 h, in which a total of 20 mL of 0.084 M (1.68 mmol) dimethydioxirane and 148 mg (0.840 mmol) of **1a** were employed. ^1H NMR (400 MHz, CD_2Cl_2, –40 °C): δ = 1.78 (s, 3H), 1.81 (s, 3H), 3.79 (s, 3H), 6.47–6.52 (m, 2H), 7.15–7.20 (m, 1H). ^{13}C NMR (100 MHz, CD_2Cl_2, –40 °C): δ = 13.9 (q), 14.0 (q), 55.2 (q), 66.9 (s), 94.7 (s), 103.4 (d), 103.6 (d), 116.1 (s), 130.4 (d), 157.5 (s), 160.4 (s).

2,3-Dihydro-2,3-dimethyl-2,3-epoxy-5-methoxybenzofuran (2b) and 6-(1′-Methyl-1′-acetylmethylene)-4-methoxy-2,4-cyclohexadienone (3b). A mixture of **2b** and **3b**, ratio 34:66, was obtained quantitatively by following the above procedure at –78 to –20 °C for 2.5 h, in which a total of 25 mL of a 0.056 M (1.40 mmol) dimethyldioxirane solution and 176 mg (1.00 mmol) of **1b** were employed. For **2b**: ^1H NMR (400 MHz, CD_2Cl_2, –20 °C) δ = 1.54 (s, 3H), 1.63 (s, 3H), 3.58 (s, 3H), 6.60–6.65 (m, 2H), 6.90–6.94 (m, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2, –20 °C) δ = 11.8 (q), 14.0 (q), 55.3 (q), 67.0 (s), 95.7 (s), 109.5 (d), 111.4 (d), 115.0 (d), 130.9 (d), 154.3 (s), 160.7 (s). For **3b**: ^1H NMR (400 MHz, CD_2Cl_2, –20 °C) δ = 1.94 (s, 3H), 2.01 (s, 3H), 3.56 (s, 3H), 5.95 (d, J = 3.0 Hz, 1H), 6.10 (d, J = 10.1 Hz, 1H), 6.84 (dd, J_1 = 10.1 Hz, J_2 = 3.0 Hz, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2, –20 °C) δ = 17.1 (q), 26.9 (q), 55.5 (q), 98.7 (d), 128.4 (s), 129.5 (d), 140.0 (d), 153.7 (s), 156.5 (s), 184.9 (s), 206.6 (s).

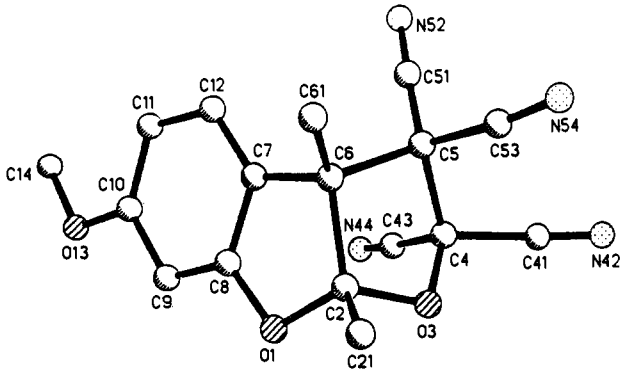
6-(1′-Methyl-1′-acetylmethylene)-3-methoxy-2,4-cyclohexadienone (3c) was obtained quantitatively by following the above procedure at –78 to –20 °C for 2 h, in which a total of 20 mL of 0.072 M (1.40 mmol) dimethyldioxirane and 176 mg (1.00 mmol) of **1c** were employed. ^1H NMR (400 MHz, CD_2Cl_2, –40 °C): δ = 2.15 (s, 3H), 2.20 (s, 3H), 3.76 (s, 3H), 5.63 (d, J = 2.4 Hz, 1H), 6.24 (dd, J_1 = 10.1 Hz, J_2 = 2.4 Hz, 1H), 7.10 (d, J = 10.1 Hz, 1H). ^{13}C NMR (100 MHz, CD_2Cl_2, –40 °C): δ = 17.2 (q), 26.9 (q), 56.1 (q), 101.2 (d), 121.5 (d), 126.8 (s), 129.3 (d), 161.0 (s), 170.8 (s), 184.2 (s), 206.7 (s).

2,3-Dihydro-2,3-dimethyl-2,3-epoxy-7-methoxybenzofuran (2d) and 6-(1′-Methyl-1′-acetylmethylene)-3-methoxy-2,4-cyclohexadienone (3d). A mixture of **2d** and **3d**, ratio 57:43, was obtained quantitatively by following the above procedure at –78 to –20 °C for 2 h, in which a total of 25 mL of 0.050 M (1.25 mmol) dimethyldioxirane and 150 mg (0.850 mmol) of **1d** were employed. For **2d**: ^1H NMR (400 MHz, CD_2Cl_2, –40 °C) δ = 1.75 (s, 3H), 1.88 (s, 3H), 3.82 (s, 3H), 6.88–7.06 (m, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2, –40 °C) δ = 11.9 (q), 13.8 (q), 55.2 (q), 66.7 (s), 94.7 (s), 111.6 (d), 115.2 (d), 121.1 (d), 130.6 (s), 152.8 (s), 162.0 (s). For **3d**: ^1H NMR (400 MHz, CD_2Cl_2, –40 °C) δ = 2.17 (s, 3H), 2.24 (s, 3H), 3.69 (s, 3H), 6.26–6.59 (m, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2, –40 °C) δ = 17.6 (q), 26.3 (q), 55.2 (q), 111.1 (d), 118.6 (d), 123.2 (d), 129.3 (s), 144.3 (s), 162.0 (s), 179.7 (s), 206.6 (s).

Irradiation (λ > 360 nm) of Epoxides 2 and Quinone Methides 3 (General Procedure). The epoxides **2** and the quinone methides **3**, which were prepared as described above, were irradiated (ca. 0.500 mmol) in acetone at –30 °C with a sodium lamp until the solution became colorless (2–6 h). After solvent removal (–20 °C at 0.1 Torr), the product was examined by NMR spectroscopy at –50 to –30 °C.

2-Acetyl-2-methyl-4-methoxybenzoxetene (4b) was obtained quantitatively by following the above procedure. ^1H NMR (200 MHz, CD_3COCD_3, –35 °C): δ = 1.78 (s, 3H), 2.26 (s, 3H), 3.71 (s, 3H), 6.68 (dd, J = 8.3 Hz, J = 0.8 Hz, 1H), 6.68–6.82 (m, 2H). ^{13}C NMR (50 MHz, CD_3COCD_3, –35 °C): δ = 20.1 (q), 24.4 (q), 55.5 (q), 100.9 (s), 108.2 (d), 108.3 (d), 115.2 (d), 134.2 (s), 154.7 (s), 158.6 (s), 205.2 (s).

(16) (a) Royer, R.; Bisagni, E.; Hudry, A.; Cheutin, A.; Desvoye, M.-L. *Bull. Soc. Chim. Fr.* **1963**, 1003–1007. (b) Kawase, Y. *Chem. Ind. (London)* **1970**, 687–688.



8c

Figure 1. ORTEP drawing of the crystal structure for the benzofurofuran **8c**.

2-Acetyl-2-methyl-6-methoxybenzoxetene (4d) was obtained quantitatively by following the above procedure. ^{1}H NMR (200 MHz, $CDCl_3$, –50 °C): δ = 1.87 (s, 3H), 2.29 (s, 3H), 3.97 (s, 3H), 6.69–6.81 (m, 3H). ^{13}C NMR (50 MHz, $CDCl_3$, –45 °C): δ = 20.1 (q), 24.3 (q), 57.5 (q), 102.8 (s), 113.2 (d), 116.5 (d), 122.0 (d), 135.1 (s), 141.7 (s), 150.6 (s), 205.5 (s).

2,3-Dihydro-3-methylene-4-methoxy-2-benzofuranol (5a). A solution of epoxide **2a** (91.0 mg, 0.500 mmol) in 0.6 mL of $CDCl_3$ was allowed to stand over a period of 12 h at –30 to 20 °C. After evaporation of the solvent (20 °C at 15 Torr), the residue was purified by column chromatography (silica gel, Et_2O/pentane) to yield 57.0 mg (63%) of **5a** as a pale yellow oil. IR (CCl_4): ν = 3550, 2940, 2895, 2830, 1580, 1430, 1360, 1330, 1225, 1100 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.67 (s, 3H), 3.87 (s, 1H), 3.91 (s, 3H), 5.35 (s, 1H), 5.87 (s, 1H), 6.43–6.48 (m, 1H), 7.13–7.21 (m, 2H). ^{13}C NMR (63 MHz, $CDCl_3$): δ = 26.7 (q), 55.4 (q), 103.0 (d), 103.2 (d), 107.8 (t), 109.1 (s), 110.5 (s), 131.4 (d), 147.6 (s), 157.3 (s), 163.3 (s). Anal. Calcd for $C_{11}H_{12}O_3$ (192.2): C, 68.73; H, 6.29. Found: C, 68.53; H, 6.23.

2,3-Dihydro-3-methylene-6-methoxy-2-benzofuranol (5c) and 3-(2′-Hydroxy-4′-methoxyphenyl)-3-buten-2-one (5′c). A solution of the quinone methide (192 mg, 1.00 mmol) in 1 mL of CD_2Cl_2 was allowed to stand over a period of 12 h at –30 to 20 °C. After evaporation of the solvent (20 °C at 15 Torr), the residue was purified by column chromatography (silica gel, Et_2O/pentane) to yield 179 mg (93%) of the 74:26 tautomeric mixture of **5c**/**5′c** as a pale yellow powder, mp 55–56 °C. IR (CCl_4): ν = 3600, 3005, 2955, 1710, 1625, 1240 cm^{-1}. ^{1}H NMR (250 MHz, CD_3COCD_3) for **5c**: δ = 1.60 (s, 3H), 3.78 (s, 3H), 5.09 (s, 1H), 5.42 (s, 1H), 6.02 (s, 1H), 6.38 (d, J = 2.3 Hz, 1H), 6.48 (dd, J_1 = 8.3 Hz, J_2 = 2.3 Hz, 1H), 7.35 (d, J = 8.3 Hz, 1H). For **5′c**: δ = 2.27 (s, 3H), 3.75 (s, 3H), 5.62 (s, 1H), 5.99 (s, 1H), 6.45–6.53 (m, 2H), 7.09 (d, J = 9.0 Hz, 1H), 8.65 (s, 1H). ^{13}C NMR (63 MHz, CD_3COCD_3) for **5c**: δ = 27.3 (q), 55.7 (q), 96.3 (d), 101.8 (t), 108.0 (d), 110.7 (s), 117.7 (s), 122.7 (d), 149.8 (s), 161.7 (s), 163.6 (s). For **5′c**: δ = 27.5 (q), 55.4 (q), 102.3 (d), 105.9 (d), 119.7 (s), 123.4 (t), 131.8 (d), 149.0 (s), 156.1 (s), 162.0 (s), 200.5 (s). MS (70 eV): m/z (relative intensity) = 192 (9) [M$^+$], 149 (13), 121 (9), 88 (6). Anal. Calcd for $C_{11}H_{12}O_3$ (192.2): C, 68.73; H, 6.29. Found: C, 68.42; H, 6.48.

2,3-Dihydro-3-methylene-7-methoxy-2-benzofuranol (5d) and 3-(2′-Hydroxy-5′-methoxyphenyl)-3-buten-2-one (5′d). (a) A solution of 91.0 mg (0.473 nmol) of benzoxetene **4d** in 0.6 mL of $CDCl_3$ was allowed to stand over a period of 2 h at 20 °C. After evaporation of the solvent (20 °C at 15 Torr), the residue was purified by column chromatography (silica gel, Et_2O/petroleum ether) to yield 46.0 mg (51%) of the 22:78 mixture of **5d** and **5′d** as a colorless oil. (b) About the same ratio of **5d** and **5′d** was isolated when a mixture of epoxide **2d** and quinone methide **3d** was allowed to stand for 2 h at 20 °C. IR (CCl_4): ν = 3530, 3000, 2960, 1680, 1580, 1465, 1435, 1350, 1275, 1220, 1060 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$) for **5d**: δ = 1.74 (s, 3H), 3.22 (s, 1H), 3.90 (s, 3H), 5.31 (s, 1H), 5.59 (s, 1H), 6.88–702 (m, 3H). For **5′d**: δ = 2.37 (s, 3H), 3.90 (s, 3H), 5.83 (d, J = 1 Hz, 1H), 5.92 (s, 1H), 5.95 (d, J = 1 Hz, 1H), 6.88–7.02 (m, 3H). ^{13}C NMR (63 MHz, $CDCl_3$) for **5d**: δ = 26.5 (q), 56.0 (q), 105.5 (t), 109.4 (s), 113.2 (d), 113.5 (d), 119.3 (s), 121.6 (d), 144.9 (s), 147.9 (s), 149.0. For **5′d**: δ = 27.3 (q), 55.9 (q), 110.7 (d), 119.8 (d), 122.4 (s), 124.7 (d), 125.7 (t), 142.9 (s), 146.5 (s), 147.0 (s), 200.0 (s). Anal. Calcd for $C_{11}H_{12}O_3$ (192.2): C, 68.73; H, 6.29. Found: C, 68.94; H, 6.41.

Methanol Trapping of Epoxides 2 and Quinone Methides 3 (General Procedure). A solution of epoxide **2** (ca. 1 mmol) or quinone methide **3** (ca. 1 mmol) in 5 mL of absolute CH_2Cl_2 was treated at –78 °C with 5 mL of absolute methanol. The reaction mixture was stirred for 0.5 h at this temperature, and the solvent was evaporated (20 °C at 15 Torr). The residue was purified by column chromatography (silica gel, Et_2O).

2,3-Dihydro-2,3-dimethyl-3,4-dimethoxy-2-benzo[*b*]furanol (6a). Treatment of 50.0 mg (0.260 mmol) of epoxide **2a** with 1 mL of methanol by following the above procedure yielded 53.0 mg (87%) of **6a** (dr = 93:7) as a colorless liquid. IR (CCl_4): ν = 3560, 3455, 2960, 2900, 2800, 1580, 1470, 1440, 1225, 1080, 1055, 895, 850 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$) for **6a** (main isomer): δ = 1.44 (s, 3H), 1.61 (s, 3H), 3.21 (s, 3H), 3.83 (s, 3H), 5.23 (s, 1H), 6.38–6.56 (m, 2H), 7.14–7.23 (m, 1H). For **6a** (minor isomer): δ = 1.46 (s, 3H), 1.68 (s, 3H), 3.49 (s, 3H), 3.89 (s, 3H), 5.01 (s, 1H), 6.42–6.63 (m, 2H), 7.13–7.21 (m, 1H). ^{13}C NMR (63 MHz, $CDCl_3$): δ = 16.3 (q), 16.5 (q), 21.6 (q), 21.7 (q), 51.7 (q), 51.9 (q), 55.2 (q), 55.3 (q), 81.9 (s), 85.4 (s), 102.9 (d), 103.0 (d), 103.9 (d), 104.3 (d), 112.3 (s), 113.6 (s), 117.5 (s), 118.2 (s), 131.5 (d), 131.6 (d), 158.6 (s), 158.8 (s), 158.9 (s), 159.6 (s). Anal. Calcd for $C_{12}H_{16}O_4$ (224.2): C, 64.27; H, 7.19. Found: C, 64.52; H, 7.47.

2,3-Dihydro-2,3-dimethyl-3,5-dimethoxy-2-benzo[*b*]furanol (6b) and 3-(5′-Methoxy-2′-hydroxyphenyl)-3-methoxybutan-2-one (6′b). Treatment of 100 mg (0.520 mmol) of epoxide **2b** and quinone methide **3b** with 5 mL of methanol by following the above procedure yielded 67.0 mg (52%) of the 80:20 tautomeric mixture of the diastereomers (dr = 78:22) **6b** and **6′b** as a colorless liquid. IR (CCl_4): ν = 3450, 2950, 2900, 1690, 1460, 1225, 1095, 1075, 1010, 890 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$) for **6b** (main isomer): δ = 1.39 (s, 3H), 1.41 (s, 3H), 3.08 (s, 3H), 3.71 (s, 3H), 5.09 (s, 1H), 6.58–6.84 (m, 3H). For **6b** (minor isomer): δ = 1.48 (s, 3H), 1.64 (s, 3H), 2.96 (s, 3H), 3.18 (s, 1H), 3.71 (s, 3H), 6.58–6.84 (m, 3H). For **6′b**: δ = 1.58 (s, 3H), 2.07 (s, 3H), 3.24 (s, 3H), 3.71 (s, 3H), 6.58–6.84 (m, 3H), 7.78 (s, 1H). ^{13}C NMR (63 MHz, $CDCl_3$): δ = 16.0 (q), 16.5 (q), 19.2 (q), 20.5 (q), 22.1 (q), 25.2 (q), 51.3 (q), 51.4 (q), 51.8 (q), 56.3 (2q), 56.6 (q), 81.6 (s), 84.4 (s), 88.1 (s), 111.1 (d), 111.4 (d), 111.6 (d), 112.3 (s), 112.7 (s), 113.4 (d), 115.1 (d), 115.7 (d), 115.9 (d), 118.2 (d), 118.5 (d), 124.1 (s), 128.1 (s), 129.2 (s), 145.3 (s), 147.5 (s), 149.7 (s), 151.8 (s), 152.8 (s), 154.6 (s), 206.9 (s). Anal. Calcd for $C_{12}H_{16}O_4$ (224.2): C, 64.27; H, 7.19. Found: C, 64.30; H, 7.37.

2,3-Dihydro-2,3-dimethyl-3,6-dimethoxy-2-benzo[*b*]furanol (6c) and 3-(4′-Methoxy-2′-hydroxyphenyl)-3-methoxybutan-2-one (6′c). Treatment of 300 mg (1.56 mmol) of quinone methide **3c** with 5 mL of methanol by following the above procedure yielded 267 mg (76%) of the 80:20 tautomeric mixture of the diastereomers (dr = 86:14) **6c** and **6′c** as a colorless liquid. IR (CCl_4): ν = 3630, 3540–3520, 1740, 1640, 1620, 1515, 1210, 1175 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$) for **6c** (main isomer): δ = 1.39 (s, 3H), 1.40 (s, 3H), 3.05 (s, 3H), 3.71 (s, 3H), 5.21 (s, 1H), 6.32 (d, J = 2.3 Hz, 1H), 6.38 (dd, J_1 = 8.7 Hz, J_2 = 2.3 Hz, 1H), 7.06 (d, J = 8.7 Hz, 1H). For **6c** (minor isomer): δ = 1.53 (s, 3H), 1.61 (s, 3H), 2.98 (s, 3H), 3.71 (s, 3H), 5.23 (s, 1H), 6.45–6.54 (m, 2H), 6.86–6.89 (m, 1H). For **6′c**: δ = 1.65 (s, 3H), 2.12 (s, 3H), 3.21 (s, 3H), 3.70 (s, 3H), 6.45–6.54 (m, 3H), 8.30 (s, 1H). ^{13}C NMR (63 MHz, $CDCl_3$): δ = 16.0 (q), 16.8 (q), 19.0 (q), 20.2 (q), 21.9, 25.8 (q), 50.3 (q), 50.6 (q), 51.5 (q), 55.2 (2q), 55.4 (q), 80.7 (s), 84.1 (s), 88.2 (s), 96.7 (d), 97.4 (d), 102.5 (d), 106.0 (d), 106.7 (d), 109.1 (s), 113.1 (s), 113.3 (d), 118.9 (d), 119.1 (s), 120.1 (s), 123.8 (s), 125.7 (d), 128.1 (d), 149.1 (s), 155.4 (s), 156.7 (s), 156.8 (s), 159.0 (s), 162.4 (s), 198.1 (s). MS (70 eV): m/z (relative intensity) = 224 (5) [M$^+$], 192 (32), 181 (86), 149 (100). Anal. Calcd for $C_{12}H_{16}O_4$ (224.2): C, 64.27; H, 7.19. Found: C, 64.32; H, 7.27.

2,3-Dihydro-2,3-dimethyl-3,7-dimethoxy-2-benzo[*b*]furanol (6d) and 3-(3′-Methoxy-2′-hydroxyphenyl)-3-methoxybutan-2-one (6′d). Treatment of 150 mg (0.780 mmol) of epoxide **2d** and quinone methide **3d** with 5 mL of methanol by following the above procedure yielded 153 mg (80%) of the 78:22 tautomeric mixture of the diastereomers (dr = 76:24) **6d** and **6′d** as a colorless liquid. IR (CCl_4): ν = 3570, 3510, 3475, 2975, 2910, 2805, 1710, 1580, 1480, 1455, 1260, 1195, 1100, 1070, 1050, 855 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$) for **6d** (main isomer): δ = 1.48 (s, 3H), 1.50 (s, 3H), 3.13 (s, 3H), 3.85 (s, 3H), 5.19 (s, 1H), 6.83–7.08 (m, 3H). For **6d** (minor isomer): δ = 1.58 (s, 3H), 1.71 (s, 3H), 2.99 (s, 3H), 3.85 (s, 3H), 4.71 (s, 1H), 6.83–7.08 (m, 3H). For **6′d**: δ = 1.63 (s, 3H), 2.12 (s, 3H), 3.23 (s, 3H), 3.85 (s, 3H), 6.83–7.08 (m, 3H), 6.91 (s, 1H). ^{13}C NMR (63 MHz, $CDCl_3$): δ = 16.0 (q), 16.4 (q), 18.7 (q), 20.4 (q),

21.9 (q), 24.8 (q), 50.9 (q), 51.1 (q), 51.3 (q), 55.8 (q), 55.9 (q), 56.0 (q), 81.2 (s), 81.8 (s), 82.1 (s), 111.0 (d), 112.1 (d), 113.0 (d), 113.3 (s), 113.7 (d), 117.1 (d), 117.2 (d), 119.1 (d), 119.7 (d), 120.4 (d), 121.4 (s), 125.3 (s), 128.0 (s), 128.6 (s), 143.6 (s), 144.6 (s), 144.9 (s), 145.7 (s), 146.2 (s), 147.4 (s), 207.6. Anal. Calcd for $C_{12}H_{16}O_4$ (224.2): C, 64.27; H, 7.19. Found: C, 64.16; H, 6.96.

Reaction of Epoxides 2 or Quinone Methides 3 with Ethyl Vinyl Ether (General Procedure). A solution of epoxide **2** or quinone methide **3** (0.68–1.37 mmol) in 2 mL of absolute CH_2Cl_2 was charged with a large excess of ethyl vinyl ether (5 mL) at –30 °C. The reaction mixture was stirred at this temperature for 1–4 days, the solution was allowed to warm up to room temperature, and the solvent was evaporated (20 °C at 15 Torr). The residue was purified by column chromatography (silica gel, Et_2O/pentane).

2,3-Dihydro-4-acetyl-2-ethoxy-5-methoxy-4-methylbenzopyran (7a) (189 mg, 72%) was obtained as a colorless powder, mp 66.5–68 °C (Et_2O), by following the above procedure at –25 °C for 2 days, in which a total of 192 mg (1.00 mmol) of epoxide **2a** and 1.00 g of ethyl vinyl ether were employed. IR (CCl_4): ν = 2980, 2905, 2840, 1715, 1605, 1590, 1470, 1095, 1090 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.12 (t, 3H, J = 7.1 Hz), 1.58 (s, 3H), 1.76 (dd, J = 14.2 Hz, J = 2.3 Hz, 1H), 1.87 (s, 3H), 2.05 (dd, J = 14.2 Hz, J = 3.4 Hz, 1H), 3.05–3.95 (m, 2H), 3.74 (s, 3H), 5.35 (dd, J = 3.4 Hz, J = 2.3 Hz, 1H), 6.51–6.61 (m, 2H), 7.16 (dd, J = 8.2 Hz, 1H). ^{13}C NMR (63 MHz, $CDCl_3$): δ = 14.7 (q), 22.2 (q), 23.7 (q), 36.2 (t), 45.5 (s), 55.0 (q), 63.8 (t), 96.0 (d), 104.0 (d), 110.8 (d), 114.5 (s), 128.5 (s), 151.9 (s), 157.7 (s), 208.8 (s). Anal. Calcd for $C_{15}H_{20}O_4$ (264.4): C, 68.15; H, 7.62. Found: C, 68.64; H, 7.63.

2,3-Dihydro-4-acetyl-2-ethoxy-6-methoxy-4-methylbenzopyran (7b) (193 mg, 74%) was obtained as a colorless oil by following the above procdure at –25 °C for 2 days, in which a total of 192 mg (1.00 mmol) of epoxide **2b** and 1.00 g of ethyl vinyl ether were employed. IR (CCl_4): ν = 2960, 2920, 1700, 1490, 1345, 1200, 1110, 970, 900 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.20 (t, J = 7.1 Hz, 3H), 1.52 (s, 3H), 1.70 (dd, J = 13.7 Hz, J = 5.5 Hz, 1H), 1.97 (s, 3H), 2.59 (dd, J = 13.7 Hz, J = 4.4 Hz, 1H), 3.58 (dq, J_1 = 7.1 Hz, J_2 = 2.5 Hz, 1H), 3.76 (s, 3H), 3.89 (dq, J_1 = 7.1 Hz, J_2 = 2.5 Hz, 1H), 5.23 (dd, J = 5.5 Hz, J = 4.4 Hz, 1H), 6.64–6.87 (m, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 15.1 (q), 24.1 (q), 25.7 (q), 37.6 (t), 48.9 (s), 55.7 (q), 63.9 (t), 97.4 (d), 112.2 (d), 113.8 (d), 118.6 (d), 128.0 (s), 145.6 (s), 154.4 (s), 209.9 (s). Anal. Calcd for $C_{15}H_{20}O_4$ (264.4): C, 68.15; H, 7.62. Found: C, 68.32; H, 7.78.

2,3-Dihydro-4-acetyl-2-ethoxy-7-methoxy-4-methylbenzopyran (7c) (233 mg, 88%) was obtained as a colorless oil by following the above procedure at –30 °C for 5 days, in which a total of 192 mg (1.00 mmol) of quinone methide **3c** and 1.00 g (69.0 mmol) of ethyl vinyl ether were employed. IR (CCl_4): ν = 3005, 2960, 1730, 1630, 1595, 1520, 1455, 1365, 1260, 1210, 1180, 1150, 1135, 1120, 1060 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.15 (t, J = 7.0 Hz, 3H), 1.51 (s, 3H), 1.64 (J_1 = 13.6 Hz, J_2 = 3.8 Hz, 1H), 1.92 (s, 3H), 2.48 (dd, J_1 = 13.6 Hz, J_2 = 6.2 Hz, 1H), 3.58–3.95 (m, 2H), 3.71 (s, 3H), 5.19 (dd, J_1 = 6.2 Hz, J_2 = 3.8 Hz, 1H), 6.37 (d, J = 2.6 Hz, 1H), 6.48 (dd, J_1 = 8.6 Hz, J_2 = 2.6 Hz, 1H), 7.00 (d, J = 8.6 Hz, 1H). ^{13}C NMR (63 MHz, $CDCl_3$): δ = 15.0 (q), 24.4 (q), 25.6 (q), 37.7 (t), 47.9 (s), 55.1 (q), 64.1 (t), 97.5 (d), 102.6 (d), 108.1 (d), 118.1 (s), 127.6 (d), 152.8 (s), 159.9 (s), 209.3 (s). MS (70 eV): m/z (relative intensity) = 264 (9) [M$^+$], 221 (100), 175 (99), 137 (11). Anal. Calcd for $C_{15}H_{20}O_4$ (264.4): C, 68.15; H, 7.62. Found: C, 68.01; H, 7.57.

2,3-Dihydro-4-acetyl-2-ethoxy-8-methoxy-4-methylbenzopyran (7d) (166 mg, 92%) was obtained as colorless needles, mp 53–54 °C (pentane), by following the above procedure at –30 °C for 5 days, in which a total of 131 mg (0.680 mmol) of a 47:53 mixture of epoxide **2d** and quinone methide **3d** and 1.00 g of ethyl vinyl ether were employed. IR (CCl_4): ν = 2995, 2975, 1715, 1590, 1480, 1360, 1270, 1230, 1060, 990 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.11 (t, J = 7.1 Hz, 3H), 1.47 (s, 3H), 1.67 (dd, J_1 = 13.8 Hz, J_2 = 4.8 Hz, 1H), 1.87 (s, 3H), 2.50 (dd, J_1 = 13.8 Hz, J_2 = 4.2 Hz, 1H), 3.45–3.95 (m, 2H), 3.79 (s, 3H), 5.34 (dd, J_1 = 4.8 Hz, J_2 = 4.2 Hz, 1H), 6.66 (dd, J_1 = 7.7 Hz, J_2 = 1.6 Hz, 1H), 6.76 (dd, J_1 = 8.6 Hz, J_2 = 1.6, 1H), 6.83–6.89 (m, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 15.0 (q), 24.4 (q), 25.6 (q), 37.2 (t), 48.4 (s), 55.9 (q), 64.2 (t), 97.4 (d), 110.87 (d), 118.7 (d), 121.4 (d), 127.8 (s), 140.9 (s), 149.4 (s), 209.9 (s). MS (70 eV): m/z (relative intensity) = 264 (37) [M$^+$], 221 (100), 175 (96), 105 (11). Anal. Calcd for $C_{15}H_{20}O_4$ (264.4): C, 68.15; H, 7.62. Found: C, 68.45; H, 7.75.

3a,7b-Dihydro-3a,7b-dimethyl-2,2,3,3-tetracyanobenzofurofuran (8c). Reaction of quinone methide **3c** with tetracyanoethylene (TCNE): A solution of 192 mg (1.00 mmol) of quinone methide **3c** in 5 mL of absolute CH_2Cl_2 was treated drop by drop at –78 °C with a solution of 128 mg (1.00 mmol) of tetracyanoethylene in 5 mL of absolute acetone. The reaction mixture was stirred for 0.5 h at this temperature, the solution was allowed to warm up to room temperature, and the solvent was evaporated (20 °C at 15 Torr). After purifying the residue by column chromatography (silica gel, Et_2O/petroleum ether), 144 mg (45%) of a colorless powder was obtained, mp 142–143 °C. IR (CCl_4): ν = 2265, 1610 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.83 (s, 3H), 1.86 (s, 3H), 3.82 (s, 3H), 6.51 (d, J = 2.3 Hz, 1H), 6.72 (dd, J = 8.7 Hz, J = 2.3 Hz, 1H), 7.41 (d, J = 8.7 Hz, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.1 (q), 21.8 (q), 55.8 (q), 56.0 (s), 60.9 (s), 70.5 (s), 97.1 (d), 107.4 (s), 107.9 (s), 108.9 (s), 109.1 (s), 110.7 (d), 113.2 (s), 123.2 (s), 125.6 (d), 159.0 (s), 164.1 (s). MS (70 eV): m/z (relative intensity) = 320 (12) [M$^+$], 177 (100), 161 (5), 135 (5). Anal. Calcd for $C_{17}H_{12}N_4O_3$ (320.3): C, 63.74; H, 3.77; N, 17.49. Found: C, 63.51; H, 3.76; N, 17.28.

9-Acetyl-3,5-dimethoxy-9-methyl-1-(1′-acetyl-1′-methylmethylene)-9,9a-dihydro-1*H*-xanthen-2(4a*H*)-one (9d). A solution of a mixture of epoxide **2d** and quinone methide **3d** (163 mg, 0.850 mmol; ratio 57:43) in 0.6 mL of $CDCl_3$ was allowed to warm up for 24 h from –20 to 20 °C. After evaporation of the solvent (20 °C at 15 Torr), the residue was purified by column chromatography (silica gel, pentane/AcOEt) to yield 86.0 mg (53%) of dimer **6d** as a colorless powder, mp 158–159 °C. IR (CCl_4): ν = 3000, 2915, 1715, 1685, 1635, 1590, 1480, 1365, 1265, 1215, 1130, 1090, 1065 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.39 (s, 3H), 1.84 (s, 3H), 1.95 (s, 3H), 2.35 (s, 3H), 3.51 (s, 3H), 3.92 (s, 3H), 3.93–3.97 (m, 1H), 5.57 (dd, J_1 = 6.1 Hz, J_2 = 1.6 Hz, 1H), 5.64 (brs, 1H), 6.55–6.58 (m, 1H), 6.84 (d, J = 7.6 Hz, 1H), 6.90–6.97 (m, 1H). ^{13}C NMR (63 MHz, $CDCl_3$): δ = 17.3 (q), 22.3 (q), 25.6 (q), 28.2 (q), 40.1 (d), 51.0 (s), 55.6 (q), 55.8 (q), 69.9 (d), 109.9 (d), 115.4 (d), 119.2 (d), 122.0 (d), 126.1 (s), 126.4 (s), 140.3 (s), 149.3 (s), 152.3 (s), 154.7 (s), 181.6 (s), 206.9 (s), 208.4 (s). MS (70 eV): m/z (relative intensity) = 384 (16) [M$^+$], 192 (29), 177 (100), 134 (36). Anal. Calcd for $C_{22}H_{24}O_6$ (384.4): C, 68.74; H, 6.29. Found: C, 68.74; H, 6.36.

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