Electrochemical Epoxidation and Carbon-Carbon Bond Cleavage for the Preparation of 3-Methyl-4-oxo-2-phenyl-4*H*-1-benzopyran-8-carboxylic Acid from 3-Methyl-2-phenyl-8-(1-propenyl)-4*H*-1-benzopyran-4-one

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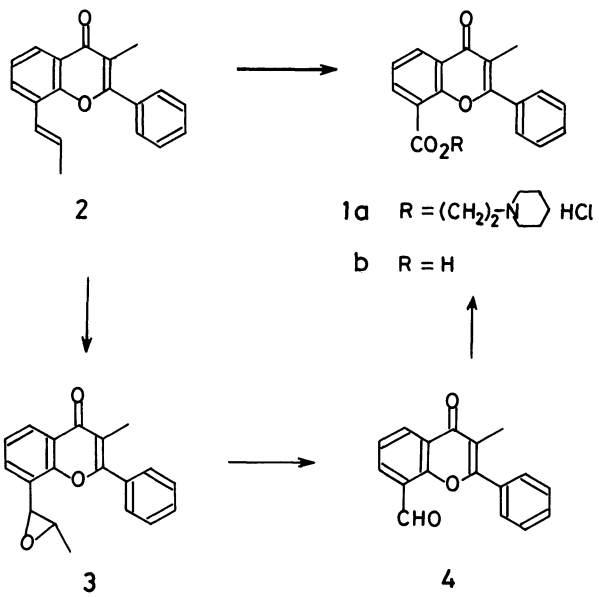
Electrooxidative carbon-carbon bond cleavage is useful for the preparation of 3-methyl-4-oxo-2-phenyl-4*H*-1-benzopyran-8-carboxylic acid (**1b**) from 3-methyl-2-phenyl-8-(1-propenyl)-4*H*-1-benzopyran-4-one (**2**). Olefin **2** was transformed into 3-methyl-8-(1,2-epoxypropyl)-3-methyl-2-phenyl-4*H*-1-benzopyran-4-one (**3**) by the electrochemical bromohydrination in an MeCN-H_2O-H_2SO_4-NaBr-(Pt) system followed by treatment of aqueous sodium hydroxide (94%). The epoxide **3** was electrooxidized in an MeOH-H_2SO_4-(C) system, affording 8-formyl-3-methyl-2-phenyl-4*H*-1-benzopyran-4-one (**4**) in 83% yield. Hydrogen peroxide oxidation of **4** in refluxing 2-butanone gave **1b** in 86% yield.

Among the flavone derivatives, 2-piperidinoethyl 3-methyl-4-oxo-2-phenyl-4*H*-1-benzopyran-8-carboxylate (**1a**) has been used as a drug for prostatitis.[1] Several syntheses have been proposed where carboxyl group of salicylic acid was employed as a source of 8-carboxyl group of **1b**.[2] Carbon-carbon bond cleavage methods of propenyl group of 3-methyl-2-phenyl-8-(1-propenyl)-4*H*-1-benzopyran-4-one (**2**)[3] and 1-(3-propenyl-2-hydroxyphenyl)propanone with potassium permanganate and dichromate[4,5] are also known. Unfeasibility of the waste heavy metal in industry prompted us to study non-heavy metal oxidation method.

Chemoselective electrooxidative cleavage of a carbon-carbon double bond of the propenyl group would be promising. However, very few example has been known so far on one-step carbon-carbon double bond cleavage. Electrooxidation of stilbene[6] in an MeOH-NH_4Cl-(Pt) system and isoeugenol[7] in an H_2O-KOH-(PbO_2) system give the corresponding aromatic aldehyde in 45 and 77% yield, respectively. Yield of the reaction is not satisfactory and alkaline media are not usable for the present purpose because of instability of **2** in the media. Oxygenation of carbon-carbon double bond followed by carbon-carbon bond cleavage leading to aldehyde is an alternative method. Dimethoxy compounds[8] and α-hydroxy ketones[9] are electrochemically cleaved but their preparation from olefins is not accessible. 1,2-Diols and epoxides are promising precursors of the desired aldehydes and can be prepared from the corresponding halohydrins whose electrochemical preparations are intensively studied. On this basis, we have studied an electrochemical preparation and carbon-carbon bond cleavage of epoxide **3** and glycol **6a**, as precursors of **1b**. (Scheme 1).



Scheme 1.

Electrooxidation of **2**. The olefin **2** was prepared as described in literatures.[10] Aqueous acetonitrile containing sodium bromide was found to be an excellent medium for the epoxidation of isoprenoids,[11] cyclohexene,[12] and isosafrole.[13] Because of the low solubility of **2** in aqueous acetonitrile, tetrahydrofuran was employed as a cosolvent. In an MeCN-THF-H_2O (5:2:2)-NaBr-(Pt) system, a constant-current-density electrolysis (3.3 mA cm^{-2}) was conducted at room temperature in an undivided cell, affording **3** in 48% yield along with the dibromide **5a** in 9% yield. When 5—10 F mol^{-1} of electricity were passed, the starting material **2** was consumed completely but the material balance was poor due to the formation of the unidentified products. The reactivity of the double bond of propenyl group of **2** was found to be lower than those of isoprenoids and isosafrole due to meta-carbonyl group. Therefore, pH of the electrolysis solution was kept at an acidic side to affect bromohydrination. The result is shown in Fig. 1.

Electrochemical bromohydrination occurs chemoselectively at the double bond of propenyl group. Yield of **5b** increased sharply and reached to an maximum value (88%) and the amount of electricity required for the conversion of **2** was saved as increase of the concentration of sulfuric acid. Interestingly, the formation of **5a** could be suppressed in a higher concentration of sulfuric acid. [Yield % **3**, **5a**, and **5b** (con-

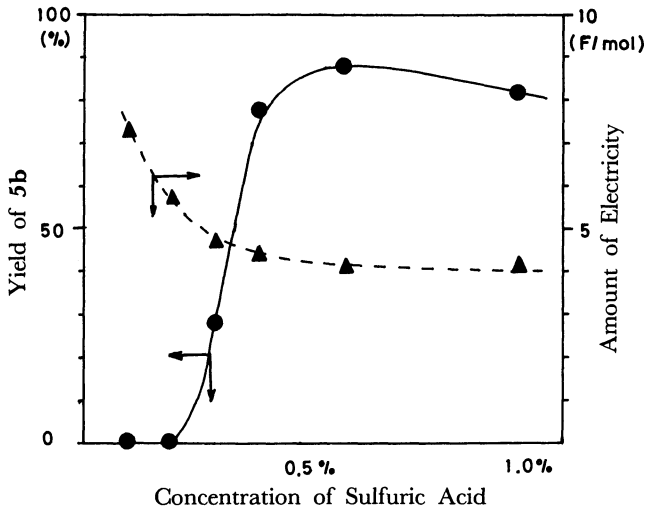


Fig. 1. Effect of the concentration of sulfuric acid for the yield of 5b and the amount of electricity in bromohydrination of **2** in an MeCN-THF-aq H_2SO_4-NaBr-(Pt) system.

centration of sulfuric acid %), 40, 32, 0 (0.1), and 0, 10, 88 (0.6)]. At 45 °C, **2** was soluble in MeCN-aq H_2SO_4 and converted to **5b** effectively in the highest chemical yield and current efficiency (93%, 2.9 F mol^{-1}).

Concentration of sodium bromide is also important. In the epoxidation of isoprenoids, bromide ion is regenerated in situ after epoxidation and thus 0.1—0.5 molar equivalent of sodium bromide to olefin is suitable so as to suppress the formation of the dibromides.[11] On the contrary to this, isosafrole **7** was efficiently electroepoxidized in the presence of 3—4 molar equivalent of sodium bromide because the dibromide **8a** was spontaneously hydrolyzed to the bromohydrin **8b** and finally converted to the epoxide *in situ* under the electrolysis conditions.[13] Hydrolysis of **5a** to **5b** was slow under the electrolysis conditions and therefore, the use of excess amount of sodium bromide should be avoided to minimize dibromination.

The base-catalyzed ring closure of **5b** to **3** proceeded smoothly. Thus, after electrochemical bromohydrination the electrolysis mixture was alkalined with 1 ml of 1 M sodium hydroxide and stirred at room temperature for 1 h, affording **3** in 94% yield.

Electrolysis of 3 and 6a. Glycol **6a** was obtained in 94% yield by the acidcatalyzed ring opening of **3** in THF-10% aq H_2SO_4 at room temperature for 11 h. The electrooxidative carbon-carbon bond cleavage of glycols has been examined in MeOH-Et_4NOTs for cyclic glycols,[14] in MeOH-NaOH for 1,1,2,2-tetraphenyl-1,2-ethanediol,[15] and in H_2O-$NaIO_4$-H_2SO_4 for 2,3-butanediol.[16] At first, electrooxidation of **6a** was examined in an MeCN-aq H_2SO_4-(Pt) system. But, unfortunately the electrooxidative cleavage of **6a** gave **4** in only 60—70% yield. Meanwhile, electrolysis in an MeOH-H_2SO_4-(C) system, the yield of **4** was improved to 91%. At 60 °C with a lower sulfuric acid concentration in MeOH, acetal **9** was formed exclusively (97%). The acetal **9** can be hydrolyzed to **4** in THF-aq H_2SO_4 almost quantitatively.

Comparison of the electrooxidative cleavage of **6a** with the chemical oxidant induced cleavage is shown in Table 1, which clearly reveals the prominent aspect of the electrolysis. Oxidation with sodium periodate proceeds smoothly under very mild conditions. However, the use of the expensive reagent is not economically feasible. Cobalt(II) acetate-catalyzed air oxidation[17] and calcium hypochlorite oxidation[18] under neutral conditions resulted in a disappointed yield.

Next, a direct cleavage of carbon-carbon bond of epoxide **3** was studied. Epoxide **3** was readily and quantitatively transformed into methoxy alcohol **6b** in MeOH-aq H_2SO_4 which was then electrolyzed *in situ*. Acetal **9** was a major product (83%) and **10b** was produced as a side product (8%). Comparison between entries 3 and 4, and entries 6 and 7 (Table 1) indicates that methoxylation on 3-methyl group took place partially at a higher current density. Presumably, electrooxidation of 2-phenyl group would compete with

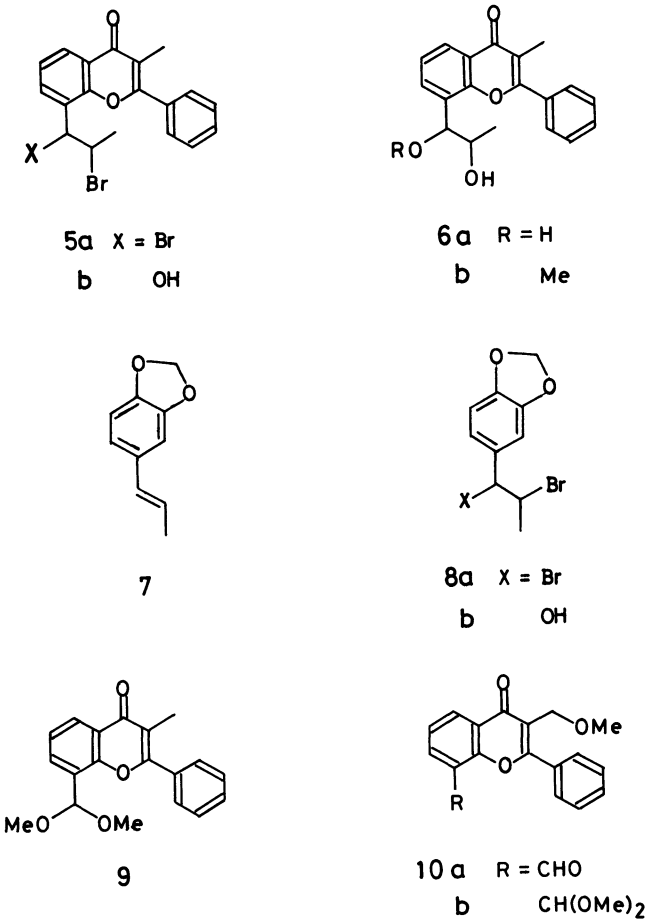
Table 1. Electrochemical and chemical oxidative transformation of **6a** and **3** into **4** or **9**

Entry	Substrate	Oxidation Methods and Conditions	F/mol	mA/cm²	Product/%[a]			
					4	**9**	**10a**	**10b**
		Electrolysis[d]						
1	**6a**	MeCN-H_2O-0.2 eq H_2SO_4-Et_4NOTs (50 °C)	7.2	3.3	68			
2		MeOH-0.8 eq H_2SO_4 (r.t.)	3.7	1.7	91[b]			
3		MeOH-0.5 eq H_2SO_4 (r.t.)	7.0	0.6	86[b]			
4		MeOH-0.5 eq H_2SO_4 (50 °C)	3.0	3.3	74[b]		6	
5		MeOH-0.15 eq H_2SO_4 (60 °C)	5.6	0.6		97[c]		
6	**3**	MeOH-0.15 eq H_2SO_4 (60 °C)	11.0	0.7		83[c]		8
7		MeOH-0.03 eq H_2SO_4 (60 °C)	4.9	1.7		77[c]		13
		Chemical Oxidation						
8	**6a**	$NaIO_4$, MeOH-H_2O (0—3 °C)[e]			82			
9		$Co(OAc)_2$-O_2, DMF (110 °C)[f]			69			
10		$Ca(ClO)_2$, MeOH-H_2O (65 °C)[g]			27			

a) Isolated yield. b) The mixture was worked up without neutralization. c) After electrolysis, the mixture was neutralized with aq $NaHCO_3$. d) Mole equivalent of H_2SO_4 to substrate. e) 2 eq of $NaIO_4$ to **6a** for 1.5 h. f) 0.3 mole eq of $Co(OAc)_2$ to **6a** for 26 h. g) 4 mole eq of $Ca(ClO)_2$ to **6a** for 7 h.

that of the glycol moiety. Current efficiency of the conversion of **6b** to **9** is lower than that of **6a** to **9**, suggesting the lower reactivity of **6b** than **6a** (entries 5 and 6). In fact, when a 1:1 mixture of **6a** and **6b** was electrolyzed in an MeOH–aq H_2SO_4–(Pt) system (2 mA for 2 d, 3 F mol^{-1} on the basis of a total amount of **6a** and **6b**, **6a** was smoothly converted to **9** in 84% yield, while **6b** was recovered intact (98%).

Oxidation of Aldehyde 4 to Carboxylic Acid 1b. Although electrooxidation of benzaldehyde provides benzoic acid, oxidation of **4** in an MeOH–aq H_2SO_4–(C) system failed and methoxylation at 3-methyl group exclusively occurred leading to the formation of **10b** in 52% yield. In the electrolysis system, the initial electron transfer from 2-phenyl group rather than the trisubstituted aromatic nucleus and the following deprotonation from 3-methyl group would generate a conjugated methyl radical, which suffers methoxylation leading to **10b** by the further one-electron oxidation. Therefore, any oxidations where an initial step occurs on the formyl group rather than aromatic nucleus must be chosen for the present purpose and also because of the instability of **4** in alkaline media, oxidation conditions must be neutral or acidic. Oxidation of **4** with hydrogen peroxide in refluxing 2-butanone proceeded slowly and gave **1b** in 86% yield where supply of hydrogen peroxide at regular time intervals was useful. Nitric acid oxidation of **4** in refluxing benzene also provided **1b** in 85% yield in which concentration of nitric acid plays an important role [Yield (molar concentration of nitric acid); 77% (2 M), 68% (3 M), 85% (4 M), and 59% (6 M)]. Meanwhile, oxidation of **3** with ammonium vanadate–nitric acid[19] in refluxing benzene yielded a mixture of **1b** and **4** (35%).



Scheme 2.

Experimental

Melting points and boiling point are uncorrected. The IR spectra were obtained with a JASCO IRA-1 spectrometer. ^{1}H NMR were measured with a JNM FX-100 spectrometer at 100 MHz or Hitachi R-24 spectrometer at 60 MHz in $CDCl_3$ using Me_4Si as an internal standard. Elemental analysis was performed using a Yanaco Model MC-2 micro-determining apparatus. Substrate **2** were supplied from Shiono Koryo Kaisha Ltd., to which the authors are grateful. A regulated DC power was supplied by a Metronix 543B instrument for electrolysis.

8-(1,2-Epoxypropyl)-3-methyl-2-phenyl-4H-1-benzopyran-4-one (3). A mixture of **2** (100 mg, 0.36 mmol) and NaBr (41 mg, 0.4 mmol) dissolved in MeCN (7 ml)–H_2O (1.7 ml) and 1% aq H_2SO_4 (0.3 ml) was electrolyzed in a beaker type undivided cell. A constant current (10 mA, 2.92 F mol^{-1}) was passed at 45 °C for 2 h and 50 min using platinum foils (1.5×2 cm^2) as an electrode. After electrolysis, 1 M NaOH (1 ml) was added to the mixture, which was stirred at room temperature for 1 h. After evaporation of MeCN, the mixture was extracted with AcOEt. The extracts were washed with brine, dried (Na_2SO_4), and concentrated *in vacuo*. The residue was chromatographed (Wako-gel C200, benzene/AcOEt=15/1) to give **3** (99.3 mg, 94%): mp 157.4—159 °C (ether); IR (Nujol) 1632, 1600, 1590, 1136, 761,700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.48 (3H, d, J=5 Hz, CH_3), 2.18 (3H, s, CH_3), 3.40 (1H, dq, J=5 Hz and 2 Hz, CH), 4.06 (1H, d, J=2 Hz, CH), 7.17—7.80 (7H, m, ArH), 8.15 (1H, dd, J= 8 Hz and 2 Hz, ArH). Found: C, 78.02; H, 5.67. Calcd for $C_{19}H_{16}O_3$: C, 78.07: H, 5.52.

8-(2-Bromo-1-hydroxypropyl)-3-methyl-2-phenyl-4H-1-benzopyran-4-one (5b). Electrolysis of **2** was conducted in the same manner as described for **3** and the mixture was worked up as usual, affording **5b** (125.2 mg, 93%): decomposed at around 160 °C; IR (Nujol) 3300 (OH), 1614, 1595, 1395, 764, 696, 657 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.58 (3H, d, J=7 Hz, CH_3), 2.15 (3H, s, CH_3), 3.00—3.42 (1H, br s, OH), 4.40—4.70 (1H, m, CH), 5.56 (1H, d, J=4 Hz, CH), 7.10—7.75 (6H, m, ArH), 7.85 (1H, dd, J=8 Hz and 2 Hz, ArH), 8.12 (1H, dd, J=8 Hz and 2 Hz, ArH). Found: C, 61.02; H, 4.57. Calcd for $C_{19}H_{17}O_3Br$: C, 61.14; H, 4.59.

8-(1,2-Dibromopropyl)-3-methyl-2-phenyl-4H-1-benzopyran-4-one (5a); mp 128—129.4 °C (ether): IR ($CHCl_3$) 1630, 1607, 1590, 1485, 1450, 1400, 1140 cm^{-1}: ^{1}H NMR ($CDCl_3$) δ=1.79 and 2.05 (3H, d, J=7 Hz, CH_3, a ratio of diastereoisomer= 2:9), 2.20 (3H, s, CH_3), 4.50—5.10 (1H, m, CH), 5.50—5.90 (1H, m, CH), 7.20—7.95 (7H, m, ArH), 8.29 (1H, J=8 Hz and 2 Hz, ArH). Found: C, 52.39; H, 3.74. Calcd for $C_{19}H_{16}O_2Br_2$: C, 52.33; H, 3.70.

8-(1,2-Dihydroxypropyl)-3-methyl-2-phenyl-4H-1-benzopyran-4-one (6a). To a solution of **3** (708.1 mg, 2.42 mmol) in distilled THF (10 ml) was added 10% aq H_2SO_4 (4 ml) at

room temperature and the mixture was stirred for 11 h. The mixture was concentrated *in vacuo* and insoluble materials were removed by filtration. The crystals on filter were washed with water and benzene, dried *in vacuo* to give **6a** (703 mg, 94%): mp 192—193 °C (AcOEt); IR (Nujol) 3400 (OH), 1620, 1605, 1125, 1067, 1025, 763, 700, 660 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.08 (3H, d, J=8 Hz, CH_3), 2.16 (3H, s, CH_3), 4.08 (1H, m, CH), 5.36 (1H, d, J=4 Hz, CH), 7.20—7.84 (6H, m, ArH), 7.96 (1H, dd, J=8 Hz and 2 Hz, ArH), 8.22 (1H, dd, J=8 Hz and 2 Hz, ArH). Found: C, 73.55; H, 6.00. Calcd for $C_{19}H_{18}O_4$: C, 73.54; H, 5.85.

8-Formyl-3-methyl-2-phenyl-4H-1-benzopyran-4-one (4) and 8-Dimethoxymethyl-3-methyl-2-phenyl-4H-1-benzopyran-4-one (9): Electrolysis of 6a. A solution of **6a** (100 mg, 0.32 mmol) dissolved in H_2SO_4–MeOH solution (25 mM, 10 ml) was electrolyzed in a beaker-type undivided cell. A constant current (5 mA, 3.86 F mol^{-1}) was passed at room temperature for 6 h and 40 min with glassy carbon electrodes (1.21×2.7 cm^2). After evaporation of MeOH under reduced pressure, the residue was dissolved in AcOEt, and the solution was washed with sat. $NaHCO_3$ and brine, dried (Na_2SO_4), and concentrated *in vacuo*. The residue was chromatographed over silica-gel (Wako-gel C200, benzene/AcOEt=11/1) to give **4** (77.7 mg, 91%): mp 119—121.5 °C; IR (Nujol) 1684, 1655, 1623, 1405, 1122, 761, 698, 660 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.22 (3H, s, CH_3), 7.17—7.87 (6H, m, ArH), 8.20 (1H, dd, J=8 Hz and 2 Hz, ArH), 8.49 (1H, dd, J=8 Hz and 2 Hz, ArH), 10.64 (1H, s, CHO). Found: C, 77.18; H, 4.52. Calcd for $C_{17}H_{12}O_3$: C, 77.26; H, 4.58.

On the other hand, **6a** was electrolyzed in H_2SO_4–MeOH solution (5 mM, 10 ml) under a constant current of 0.67 mA cm^{-2} at 60 °C for 24 h (5.6 F mol^{-1}) using glassy carbon electrodes (1.2×2.5 cm^2). After electrolysis, the reaction solution was neutralized with sat. $NaHCO_3$. The usual workup provided **9** (96.7 mg, 97%): mp 136.5—137.5 °C (ether); IR (Nujol) 1644, 1486, 1404, 1115, 1060, 770, 703, 660 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.20 (3H, s, CH_3), 3.39 (6H, s, OCH_3), 5.84 (1H, s, ArCH), 7.20—7.80 (6H, s, ArH), 7.90 (1H, dd, J=8 Hz and 2 Hz, ArH), 8.24 (1H, dd, J=8 Hz and 2 Hz, ArH). Found: C, 73.38: H, 5.93. Calcd for $C_{19}H_{18}O_4$: C, 73.54; H, 5.85.

Oxidation of 6a with $NaIO_4$. A solution of $NaIO_4$ (96 mg, 0.45 mmol) in H_2O (3 ml) was dropped to **6a** (70 mg, 0.23 mmol) dissolved in MeOH (4 ml) at 0—3 °C and the mixture was stirred at the temperature for 1.5 h. Ethyl acetate extraction followed by chromatography (Wako-gel C200, benzene/AcOEt=10/1) provided **4** (49.4 mg, 82%).

Oxidation of 6a with $Co(OAc)_2$–O_2. A mixture of **6a** (100 mg, 0.32 mmol) and $Co(OAc)_2$ (17 mg, 0.096 mmol) dissolved in DMF (6 ml) was stirred under oxygen atmosphere at 110—115 °C for 26 h. After addition of water, the organic substance was extracted with AcOEt. The usual workup provided **4** (58.9 mg, 69%).

Oxidation of 6a with $Ca(OCl)_2$. A suspension of $Ca(OCl)_2$ (23 mg, 0.1 mmol) in MeCN (2 ml)–H_2O (1 ml) was added to a solution of **6a** (60 mg, 0.19 mmol) dissolved in MeCN (4 ml)–H_2O (2 ml). After vigorous stirring at 65 °C for 1 h, $Ca(OCl)_2$ (70 mg, 0.3 mmol) suspended in MeCN (2 ml)–H_2O (1 ml) was added again and the mixture was stirred for 2 h. In the same way, $Ca(OCl)_2$ (52 mg, 0.22 mmol) suspended in MeCN (1 ml)–H_2O (1 ml) was added additionally twice and the mixture was stirred for 2 h in each addition. Organic substances were extracted with AcOEt and the usual workup provided **4** (14 mg, 27%) after chromatography.

Electrolysis of 3. A solution of **3** (100 mg, 0.34 mmol) dissolved in H_2SO_4–MeOH solution (5 mM, 10 ml) was stirred at 60 °C for 40 min. And the mixture was electrolyzed under a constant current of 0.67 mA cm^{-2} at 60 °C for 48 h (10.5 F mol^{-1}) using glassy carbon electrodes. After evaporation of MeOH, the residue was dissolved in THF (3 ml). The mixture was added 10% aq H_2SO_4 (2 ml) and stirred at room temperature for 1 h, concentrated *in vacuo*, and extracted with AcOEt. The extracts were washed with sat. $NaHCO_3$ and brine, dried (Na_2SO_4), and concentrated *in vacuo*. The residue was chromatographed (Wako-gel C200, benzene/AcOEt=15/1) to give **4** (75.7 mg, 84%).

8-(2-Hydroxy-1-methoxypropyl)-3-methyl-2-phenyl-4H-1-benzopyran-4-one (6b). The acid-catalyzed ring opening of **3** as described above and the usual workup gave **6b** (quantitatively): mp 151—152 °C (ether); IR (Nujol) 3350 (OH), 1626, 1585, 1397, 1114, 763, 695, 660 cm^{-1}; ^1H NHR ($CDCl_3$) δ=1.14 (3H, d, J=6 Hz, CH_3), 2.13 (3H, s, CH_3), 2.92 (1H, br s, OH), 3.30 (3H, s, OCH_3), 3.95—4.35 (1H, m, CH), 4.85 (1H, d, J=5 Hz, ArCH), 7.20—7.90 (7H, m, ArH), 8.10 (1H, dd, J=8 Hz and 2 Hz, ArH). Found: C, 74.09: H, 6.27. Calcd for $C_{20}H_{20}O_4$: C, 74.06: H, 6.21.

After electrolysis, the reaction mixture was neutralized with sat. $NaHCO_3$. The usual workup and chromatography gave **9** (83%).

3-Methyl-4-oxo-2-phenyl-4H-1-benzopyran-8-carboxylic Acid (1b). Oxidation of 4 with Hydrogen Peroxide: To a solution of **4** (80 mg, 0.30 mmol) in 2-butanone heated to 90—95 °C, 31% of H_2O_2 (1 ml) was added four times at every 10 h intervals. After being stirred for 44 h, H_2O_2 was quenched with $NaHSO_3$. The reaction mixture was acidified with 10% HCl and extracted with AcOEt. The extracts were concentrated *in vacuo*. The residue was dissolved in sat. $NaHCO_3$ and extracted with AcOEt. The aqueous layer was acidified with 10% HCl and extracted with AcOEt. The extracts were dried (Na_2SO_4) and concentrated *in vacuo*. The residue was chromatographed over short silica-gel column (Wako-gel C200, AcOEt/benzene=3/1) to give **1b** (72.4 mg, 85%): mp 226.5—228 °C (AcOEt)(lit,[3a] 227—229 °C); IR (Nujol) 3160 (OH), 1734, 1620, 1218, 1180, 1134, 1025, 785, 763, 700, 678, 664 cm^{-1}; ^1H NMR ($CDCl_3$+CD_3OD=1:2) δ=2.23 (3H, s, CH_3), 7.30—7.65 (5H, m, ArH), 7.70—7.95 (1H, m, ArH), 8.15—8.55 (2H, m, ArH).

Oxidation of 4 with Nitric Acid. A solution of **4** (80 mg, 0.30 mmol) in benzene (2 ml) was added to 4 M HNO_3 (6 ml) and stirred vigorously at 90 °C for 49 h. The reaction mixture was extracted with AcOEt. The extracts were concentrated *in vacuo*. The residue was dissolved in sat. $NaHCO_3$ and extracted with AcOEt. The aqueous layer was acidified with 10% HCl and extracted with AcOEt. The extracts were dried (Na_2SO_4) and concentrated *in vacuo*. The residue was chromatographed over short column (Wako-gel C200, AcOEt/benzene=3/1) to give **1b** (72 mg, 85%).

8-Formyl-3-methoxymethyl-2-phenyl-4H-1-benzopyran-4-one (10a). Mp 146.7—148 °C (ether); IR (Nujol) 1690, 1660, 1623, 1090, 760, 690, 656 cm^{-1}: ^1H NMR ($CDCl_3$) δ=3.50 (3H, s, OMe), 4.37 (2H, s, CH_2), 7.10—8.00 (6H, m, ArH), 8.17 (1H, dd, J=8 Hz and 2 Hz, ArH), 8.45 (1H, dd, J=8 Hz and 2 Hz, ArH), 10.64 (1H, s, CHO). Found: C, 73.71; H, 4.90. Calcd for $C_{18}H_{14}O_4$: C, 73.46; H, 4.79.

8-Dimethoxymethyl-3-methoxymethyl-2-phenyl-4H-1-benzo-

*pyran-4-one (**10b**).* Bp 185—186 °C (6.92×10^{-1} Pa): IR(Neat 2950, 1740, 1715, 1650, 1490, 778, 705, 665 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.37 (6H, s, OMe), 3.50 (3H, s, OMe), 4.36 (2H, s, CH_2), 5.85 (1H, s, CH), 7.25—8.10 (7H, m, ArH), 8.25 (1H, dd, J=8 Hz and 2 Hz, ArH). Found: C, 73.89; H, 6.43. Calcd for $C_{20}H_{20}O_4$: C, 74.06; H, 6.21.

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