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Synthesis and Electrochemical Properties of 3-(3,6-Dioxo-1,4-cyclohexadienyl)methyl-*p*-tropoquinone. Analysis of a Four-Electron Redox System by Cyclic Voltammetry

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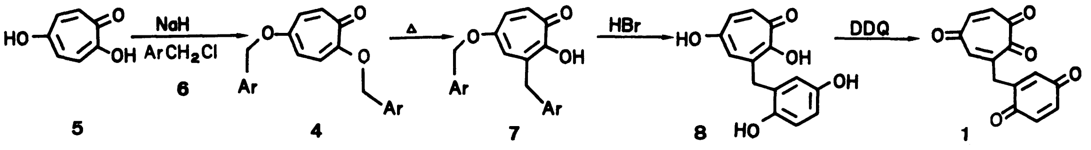
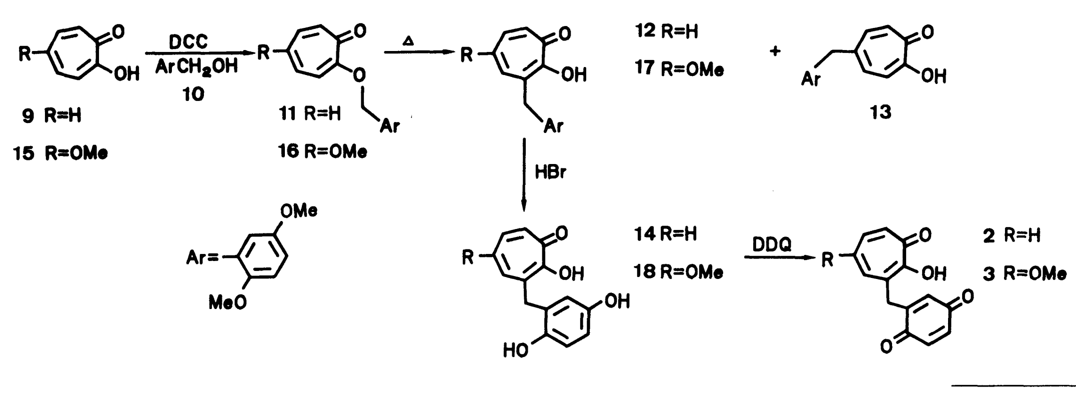
A methylene-linked bisquinone, 3-(3,6-dioxo-1,4-cyclohexadienyl)methyl-*p*-tropoquinone, was prepared from 2,5-bis(arylmethoxy)tropone by consecutive reaction, a homolytic rearrangement, subsequent debenzylation, and a DDQ-dehydrogenation. According to cyclic voltammetry, this four-electron redox system was operative, in sharp contrast to the case of the benzenoid bisquinones, via four successive one-electron transfer processes. Two other tropolone derivatives carrying *p*-benzoquinone segment were also prepared by a similar procedure. The first reduction potentials of these benzoquinones showed a slight enhancement by intramolecular hydrogen bonding.

Recently, we have measured an enhancement of the half-wave potentials due to an electron-attractive substituent of the *p*-tropoquinones;[1] in the case of 3-(*p*-hydroxybenzyl)-*p*-tropoquinone, the hydroxyl group considerably enhanced the redox potentials by an intermolecular hydrogen bonding.[2]

As one part of an electrochemical study of *p*-tropoquinones, we synthesized 3-(3,6-dioxo-1,4-cyclohexadienyl)methyl-*p*-tropoquinone (**1**), a methylene-linked bisquinone, together with 3-[(3,6-dioxo-1,4-cyclohexadienyl)methyl]tropolone and 5-methoxy-3-[(3,6-dioxo-1,4-cyclohexadienyl)methyl]tropolone (**2** and **3**). As described below, cyclic voltammetry (CV) of **1** indicated occurrence of four-times one-electron transfer processes.

When 2,5-bis(2,5-dimethoxybenzyloxy)tropone (**4**), prepared in 70% yield from 5-hydroxytropolone (**5**) and 2,5-dimethoxybenzyl chloride (**6**), was heated in decalin,[3] the thermally-transformed isomer, 3-(2,5-dimethoxybenzyl)-5-(2,5-dimethoxybenzyloxy)tropolone (**7**) was obtained in 55% yield. A debenzylation of **7** by 48% hydrobromic acid in acetic acid afforded 5-hydroxy-3-(2,5-dihydroxybenzyl)tropolone (**8**), and its DDQ (2,3-dichloro-5,6-dicyano-*p*-benzoquinone)-dehydrogenation gave desired **1**. The overall yield of **1** from **7** was 70%.





The condensation[4] of tropolone (**9**) with 2,5-dimethoxybenzyl alcohol (**10**) in the presence of dicyclohexylcarbodiimide (DCC) and copper(I) chloride gave 2-(2,5-dimethoxybenzyloxy)tropone (**11**), which was converted to 3-(2,5-dimethoxybenzyl)tropolone (**12**) and 5-(2,5-dimethoxybenzyl)tropolone (**13**) in refluxing decalin. Subsequent demethylation of **12** with concd hydrobromic acid in acetic acid afforded the hydroquinone derivative, 3-(2,5-dihydroxybenzyl)-tropolone (**14**), which was dehydrogenated with DDQ to **2**, a tropolonated *p*-benzoquinone.

Similarly, a condensation of 5-methoxytropolone

(**15**) and **10** gave the corresponding arylmethoxytropone (**16**) in 71% yield. Heating of **16** in refluxing decalin afforded 5-methoxy-3-(2,5-dimethoxybenzyl)-tropolone (**17**) in 93% yield. Hydrobromic acid-demethylation of **17** in acetic acid formed only a 5-methoxytropolone derivative, 3-(2,5-dihydroxybenzyl)-5-methoxytropolone (**18**). The dehydrogenation of **18** with DDQ gave **3**, another tropolonated *p*-benzoquinone.

The CV of **1** showed four waves. The first half-wave potential ($E_1 = -0.20$ V vs. Ag/AgCl) was just the same as the E_1 of *p*-tropoquinone (**19**),[1] indicating a negligible substituent effect due to a methylene-linked electronegative *p*-benzoquinone moiety; the second wave ($E_2 = -0.51$ V) was also similar to the $E_1 = -0.50$ V of methyl-*p*-benzoquinone (**20**).

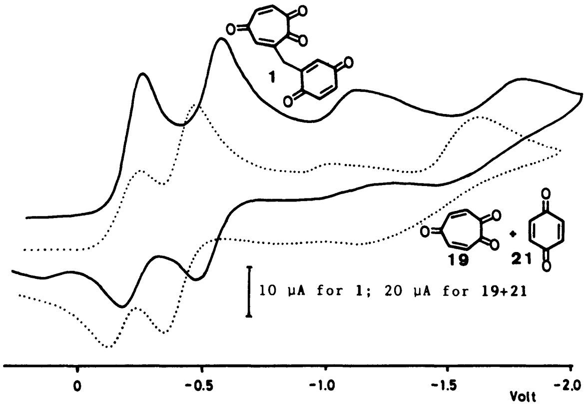


Fig. 1. The CV curve (working electrode, Pyrex-glass-sealed Pt wire; reference electrode, standard Ag/AgCl) of **1** (1.56×10^{-3} mol dm^{-3}, solid line) and a 1 : 1-mixture of **19** and **21** (1.49×10^{-3} mol dm^{-3}, dotted line) at 22—23 °C in anhydrous DMF with 0.1 M TBAF under N_2 with a scan rate of 100 mV s^{-1}.

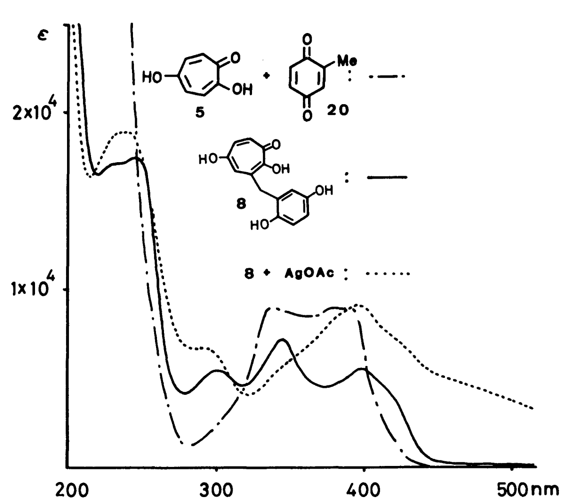
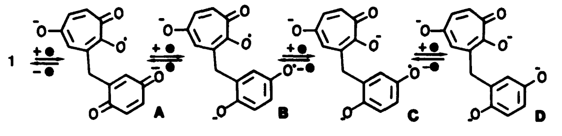
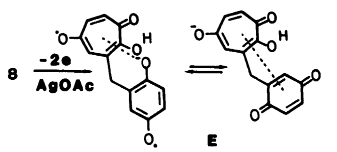


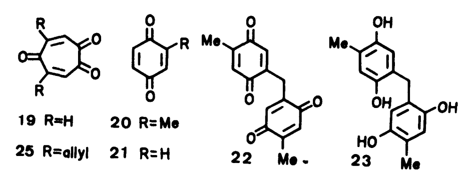
Fig. 2. Effect of AgOAc to the UV Spectrum of **8** in methanol: (——) without AgOAc; (------) in the presence of stoichiometric amount of AgOAc to produce the "Half-quinone" (**E**); (—·—) equimolar amounts of **5** and **20**.

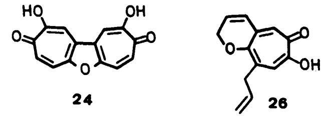
However, the intensities of the E_3 and E_4 peaks (-1.10 and -1.68 V) of **1** gradually decreased upon multiple-sweeping; finally, only the E_1 and E_2 remained at -0.21 and -0.52 V. This might be due to both or either the further chemical reaction and/or the instability of the intermediate species (**A**—**D**). On the other hand, a CV measurement of a 1 : 1-mixture of **19** and *p*-benzoquinone (**21**) showed four reproducible waves at $E_1 = -0.21$, $E_2 = -0.41$, $E_3 = -0.89$, and $E_4 = -1.46$ V. Consequently, **1** behaved as a combination of **19** and **21** in respect to CV.

The UV spectrum of **8** in the presence of silver acetate, whose amount was just equivalent to two-electron oxidation, showed a new absorption band around 430 nm. The UV spectrum of a 1 : 1-mixture of **5** and **20** showed no band around this region. Therefore, the occurrence of this absorption band indicated a charge-transfer character of the half quinone equivalent (**E**) formed in situ. Since the concentrations for the UV measurement were ca. 10^{-5} to 10^{-6} mol dm^{-3}, this must be an intramolecular charge-transfer absorption.[5] Should the two-electron reduced species (**B**) disproportionate to the deprotonated species of a half-quinone equivalent, **E**, the CV of **1** might reveal an irreversible intervention of subsequent processes due to an intramolecular side reaction. To date, there is no UV spectral evidence for the formation of either "quinhydrone" or charge-transfer complex in tropoquinones.









The peak potintials of **2** and **3** are shown in Table 1 together with those of **20** and **21**. Both show irreversible waves; particularly, their oxidation waves are hardly discernible. Nevertheless, their first reduction peaks move to a slightly more positive side than that

Table 1. The Peak Potentials/V of **2** and **3** together with Reference Quinones[a)]

Compds.	**2**	**3**	**20**	**21**
Ep1	−0.47	−0.46	−0.50	−0.44
Ep2	−1.23	−1.27	−1.58	−1.55

a) CV was measured in anhydrous DMF with 0.1 M TBAF using Pyrex glass-sealed Pt-wire as working electrode and standard Ag/AgCl as reference electrode at 22—23 °C under N_2 with a scan rate of 100 mv s^{-1}.

of **20**. This is attributable to an intramolecular hydrogen bonding.[2)]

Interestingly, bis(4-methyl-3,6-dioxo-1,4-cyclohexadienyl)methane, a bisquinone (**22**),[6)] is known to reveal two one-electron paths and one two-electron path in the formation of fully reduced bis[(2,5-dihydroxy-4-methyl)phenyl]methane (**23**); a marked difference in the reduction mode should be attributable to the structural difference of the two bisquinones.

In conclusion, this conversion of **1** to **8** via the four single-electron reduction processes constitutes a new redox system; its CV data suggested that the present bisquinone is as a strong oxidizing agent as **19**. At the same time, the appearance of a charge-transfer band in the UV spectrum might suggest a possible formation of a side product from the intermediate species, such as **B**.[7)] In fact, the electrolysis of **19** gave 2,10-dihydroxycyclohepta[*b*,*d*]furan-3,9-dione (**24**)[8)] in 44% yield under the same conditions as the CV measurement; moreover, we observed that 4,6-diallyl-*p*-tropoquinone (**25**) was electrolyzed to a cyclized derivative, 9-allyl-7-hydroxycyclohepta[*b*]pyran-6(2*H*)-one (**26**).[9)]

Experimental

The elemental analyses were performed by Miss S. Hirashima, of the Research Institute of Industrial Science, Kyushu University. The CV measurements were carried out in a standard three-electrode cell (working electrode; Pyrex glass-sealed Pt wire, reference electrode; standard Ag/AgCl) at 23°C in an anhydrous *N*,*N*-dimethylformamide (DMF) with 0.1 M tetrabutylammonium tetrafluoroborate (TBAF) under an N_2 stream with a scan rate of 100 mV s^{-1}; the values were corrected with an internal standard for the redox of a ferrocenium/ferrocene couple at +0.465 V vs. Ag/AgCl. The NMR spectra were measured by a JEOL FX 100 spectrometer in $CDCl_3$ solutions (unless otherwise specified) and the chemical shifts were expressed in δ units. The mass spectra were measured with a JEOL 01SG-2 spectrometer. The IR spectra were taken as KBr disks using a Jasco IR-A 102 spectrometer.

Preparation of 2,5-Bis(2,5-dimethoxybenzyloxy)-tropone (4). To an HMPA solution (4.5 cm^3) of **5** (300 mg), NaH (50%, 256 mg) was added under an N_2 atmosphere at 0—5°C. The mixture was then warmed to room temperature and stirred for a further 2 h at 60°C. After again cooling mixture to room temperature, an HMPA solution (2 cm^3) of **6** (853 mg) was added and stirring continued for 19 h; then, the mixture was diluted with water and the precipitates were collected by filtration and recrystallized from aqueous acetone to give **4** [yellow brown crystals, mp 123.5—125.5°C (decomp), 669 mg; 70%. Found: C, 68.20; H, 6.14%. Calcd for $C_{25}H_{26}O_7$: C, 68.48; H, 5.98%. ^1H NMR $\delta=3.72$ (3H, s), 3.76 (3H, s), 3.79 (3H, s), 3.81 (3H, s), 4.97 (2H, s), 5.22 (2H, s), 6.35 (1H, d, $J=11.5$ Hz), 6.76 (1H, d, $J=11.5$ Hz), 6.7—7.0 (6H, m), 7.10 (1H, d, $J=13$ Hz), and 7.26 (1H, d, $J=13$ Hz). ^{13}C NMR $\delta=55.7$ (2C), 55.9 (2C), 65.4, 65.8, 109.1, 111.3 (2C), 113.5, 113.8 (2C), 114.6, 116.5, 124.9, 125.3, 132.7, 137.6, 150.5, 150.8, 153.6, 153.8, 158.6, 158.9, and 179.5. IR ν: 1572, 1520, 1242, 1220, 1185, and 1042 cm^{-1}. UV λ_{max}^{MeOH}: 227 nm (ε=37900), 251 (10100, sh), 308 (11300), 329 (12400), 361 (9100, sh), and 379 (5900, sh)].

Thermal Rearrangement of 4 to 3-(2,5-Dimethoxybenzyl)-5-(2,5-dimethoxybenzyloxy)tropolone (7). A decalin solution (40 cm^3) of **4** (800 mg) was refluxed for 2 h under an N_2 atmosphere. Silica-gel column chromatography of the mixture gave **7** [pale yellow crystals, mp 101—104°C, 482 mg; 55%. Found: C, 68.31; H, 5.96%. Calcd for $C_{25}H_{26}O_7$: C, 68.48; H, 5.98%. ^1H NMR $\delta=3.68$ (3H, s), 3.70 (3H, s), 3.72 (3H, s), 3.74 (3H, s), 4.10 (2H, s), 4.93 (2H, s), 6.7—7.0 (6H, m), and 7.0—7.3 (3H, m). ^{13}C NMR $\delta=35.0$, 55.7 (2C), 55.8 (2C), 65.8, 111.4 (2C), 112.1, 113.4, 114.5, 117.1, 120.5, 120.9, 124.2, 125.1, 128.3, 128.9, 140.2, 150.8, 151.8, 153.6, 157.7, 163.8, and 170.0. IR ν: 1605, 1502, 1400, 1230, 1218, 1200, and 1049 cm^{-1}. UV λ_{max}^{MeOH}: 229 nm (ε=35100), 251 (21100, sh), 298 (8900), 333 (10800), 370 (7400), and 387 (7100)].

Hydrobromic Acid Treatment of 7 to 3-(2,5-Dihydroxybenzyl)-5-hydroxytropolone (8). An AcOH solution (15 cm^3) of **7** (576 mg) and aq HBr (48%, 15 cm^3) was refluxed for 2 h. The mixture was then diluted with water and extracted with AcOEt. The organic extract was washed with an aqueous NaCl solution, dried on Na_2SO_4, and heated in vacuo to give a residue which, by recrystallization from $CHCl_3$, gave **8** [brown crystals, mp 167—170°C, 331 mg; 97%. Found: M.W., 260.0673. Calcd for $C_{14}H_{12}O_5$: 260.0683. ^1H NMR (CD_3OD) $\delta=4.00$ (2H, s), 6.4—6.7 (3H, m), 6.92 (1H, dd, $J=11.5$, 3 Hz), 7.31 (1H, d, $J=11.5$ Hz), and 7.34 (1H, d, $J=3$ Hz). ^{13}C NMR (CD_3OD) $\delta=36.7$, 115.8, 118.0, 118.4, 122.6, 124.0, 127.8, 131.2, 145.6, 149.6, 151.7, 160.2, 163.9, and 171.9. IR ν: 3600—2400, 1375, and 1210 cm^{-1}. UV λ_{max}^{MeOH}: 231 nm (ε= 17000), 244 (17200), 300 (5400), 344 (7100), 398 (5500), and 413 (4600, sh)].

DDQ-Oxidation of 8 to 3-[(3,6-Dioxo-1,4-cyclohexadienyl)methyl]-*p*-tropoquinone (1). To an acetone solution of **8** (25.4 mg) was added DDQ (48 mg) at room temperature. After stirring for 18 h, the mixture was evaporated in vacuo, and the residue was chromatographed on a silica-gel column; **1** [yellow crystals, mp 122—125°C (decomp), 17.9 mg; 72%. Found: M.W., 256.0368. Calcd for $C_{14}H_8O_5$: 256.0369. ^1H NMR $\delta=3.64$ (2H, dd, $J=1.5$, 1 Hz), 6.65 (1H, tt, $J=1.5$, 1 Hz), 6.76 (2H, d, $J=1$ Hz), 6.82 (1H, quint, $J=1$ Hz), and 6.84 (2H, d, $J=1$ Hz). ^{13}C NMR $\delta=32.8$, 134.2, 135.2, 136.8, 137.0, 138.5, 139.5, 144.0, 144.5, 186.6, 187.0, 187.5, 188.3, and 188.7. IR ν: 1655 cm^{-1}. UV λ_{max}^{MeOH}: 245 nm (ε= 21100)] was obtained from the elution with benzene: AcOEt (10 : 1).

AgOAc-Oxidation of 8 to 1. To an acetone solution (3 cm^3) of **8** (30 mg) was added AgOAc (79 mg) at room temperature. After 5 h, the insoluble materials were filtered off, and the filtrate was evaporated in vacuo and chromatographed on a silica-gel column to give **1** [10 mg; 34%].

Preparation of 2-(2,5-Dimethoxybenzyloxy)tropone (11). To an anhydrous benzene solution (0.5 cm^3) of **10** (895 mg) was added DCC (1.13 g) and CuCl (3 mg). After being stirred at 60°C for 11 h, an anhydrous benzene solution (0.5 cm^3) of **9** (436 mg) was added to the mixture and kept at 60°C for another 18 h. The resultant precipitates were filtered off and washed with AcOEt. The combined organic portion was evaporated in vacuo and the residue was chromatographed on a silica-gel column to give **11** [pale yellow crystals, mp 71—72.5°C, 806 mg; 83%. Found: C, 70.73; H, 6.06%. Calcd for $C_{16}H_{16}O_4$: C, 70.57; H, 5.92%. ^{1}H NMR δ=3.70 (3H, s), 3.80 (3H, s), 5.24 (2H, s), and 6.6—7.2 (8H, m). ^{13}C NMR δ=55.9, 56.1, 65.9, 111.7, 114.1, 114.3, 114.7, 124.8, 128.2, 133.0, 136.6, 137.4, 150.9, 154.2, 164.8, and 181.0 IR ν: 1594, 1580, 1515, 1498, and 1284 cm^{-1}. UV λ_{max}^{MeOH}: 227 nm (ε=24900), 303 (7900), 318 (7200), 347 (5400), and 365 (3600)].

Thermal Rearrangement of 11 to 3-(2,5-Dimethoxybenzyl)tropolone (12) and 5-(2,5-Dimethoxybenzyl)tropolone (13). A decalin solution (16 cm^3) of **11** (353 mg) was refluxed for 11.5 h under an N_2 atmosphere. The resultant mixture was chromatographed on a silica-gel column to give **12** [yellow brown crystals, mp 65—67°C, 270 mg; 93%. Found: C, 70.67; H, 5.92%. ^{1}H NMR δ=3.70 (3H, s), 3.72 (3H, s), 4.12 (2H, s), 6.7—7.0 (4H, m), and 7.2—7.4 (3H, m). ^{13}C NMR δ=34.6, 55.7, 56.1, 111.7, 112.1, 117.5, 121.0, 127.4, 128.7, 136.0, 139.6, 140.3, 152.1, 153.8, 168.2, and 173.0. IR ν: 1612, 1600, 1522, 1500, 1425, 1380, 1226, 1050, and 750 cm^{-1}. UV λ_{max}^{MeOH}: 231 nm (ε=26000), 243 (24700, sh), 304 (6900, sh), 322 (7600), 356 (5900), and 367 (5800)] and **13** [yellow crystals, mp 108.5—111°C, 8.8 mg; 3%. Found: C, 70.68; H, 6.01%. ^{1}H NMR δ=3.72 (6H, s), 3.88 (2H, s), 6.6—6.8 (3H, m), 7.18 (2H, d, J=12 Hz), and 7.30 (2H, d, J=12 Hz). ^{13}C NMR δ=40.1, 55.8, 56.0, 111.8, 112.1, 117.2, 124.1 (2C), 129.4, 138.8 (2C), 142.0, 151.8, 153.9, and 171.1 (2C). IR ν: 3200, 1560, 1495, 1460, 1420, 1270, 1238, and 1214 cm^{-1}. UV λ_{max}^{MeOH}: 228 nm (ε=26500), 325 (10300), and 372 (4800, sh)] together with **3** [61.7 mg; 17%].

Demethylation of 12. An AcOH solution (10 cm^3) of **12** (378 mg) and HBr (48%, 10 cm^3) was refluxed for 1.5 h. The mixture was then diluted with water and extracted with AcOEt. The organic extract was dried on $MgSO_4$ and heated in vacuo. The residue was purified by repeated recrystallizations from a mixture of AcOEt and hexane to give **14** [yellow crystals, mp 134—136°C, 267 mg; 79%. Found: C, 68.67; H, 5.24%. Calcd for $C_{14}H_{12}O_4$: C, 68.84; H, 4.95%. ^{1}H NMR (CD_3OD) δ=4.01 (2H, s), 6.47 (1H, dd, J=8.5, 2.5 Hz), 6.56 (1H, dd, J=2.5, 1 Hz), 6.63 (1H, dd, J=8.5, 1 Hz), and 6.8—7.7 (4H, m). ^{13}C NMR (CD_3OD) δ=36.8, 115.7, 117.8, 118.4, 122.7, 127.9, 129.4, 137.9, 141.5, 143.4, 149.6, 151.7, 169.5, and 175.0. IR ν: 3600—2500, 1542, 1510, 1482, 1476, 1380, and 1210 cm^{-1}. UV λ_{max}^{MeOH}: 237 nm (ε=20000), 331 (7700), 375 (5900), and 392 (4700, sh)].

The DDQ-Oxidation of 14. An acetone solution (10 cm^3) of **14** (99.1 mg) and DDQ (105 mg) was stirred at room temperature for 4 h. The solvent was then removed by evaporation and the residue was briefly chromatographed on a silica-gel column. Yellow crystals obtained by elution from hexane-AcOEt (10 : 1) and removal of the solvent were recrystallized from benzene to give **2** [mp 99.5—101.5°C, 65.2 mg; 66%. Found: C, 69.16; H, 4.11%. Calcd for $C_{14}H_{10}O_4$: C, 69.42; H, 4.16%. ^{1}H NMR δ=3.90 (2H, d, J=1.5 Hz), 6.53 (1H, dtd, J=2, 1.5, 1 Hz), 6.65 (1H, dd, J=10, 2 Hz), 6.77 (1H, dd, J=10, 1 Hz), 6.9—7.3 (3H, m), and 7.57 (1H, d, J=9.5 Hz). ^{13}C NMR δ=34.6, 120.7, 127.7, 128.7, 133.8, 136.7, 137.0, 137.3, 141.4, 146.4, 168.1, 173.6, 187.4, and 188.0. IR ν: 3600—3300, 3200, 1650, 1548, 1420, 1295, and 1236 cm^{-1}. UV λ_{max}^{MeOH}: 243 nm (ε=37600), 327 (8600), 333 (8700), 373 (6000), and 391 (4300, sh)].

Preparation of 2-(2,5-Dimethoxybenzyloxy)-5-methoxytropone (16). A benzene solution (0.3 cm^3) of **10** (357 mg), DCC (428 mg), and CuCl (5 mg) was stirred at 60°C for 16 h under an N_2 atmosphere, to which, a benzene solution (0.5 cm^3) of **15** (213 mg) was introduced and stirred further for 10 h. The precipitates formed were filtered off and washed with AcOEt, and the residue obtained by removing organic solvents in vacuo was recrystallized from AcOEt to give **16** [yellow crystals, mp 131—132°C, 300 mg; 71%. Found: C, 67.76; H, 6.05%. Calcd for $C_{17}H_{18}O_5$: C, 67.54; H, 6.00%. ^{1}H NMR δ=3.72 (6H, s), 3.81 (3H, s), 5.23 (2H, s), 6.21 (1H, dd, J=11, 2.5 Hz), 6.74 (1H, d, J=8 Hz), 6.77 (1H, d, J=11 Hz), 6.84 (1H, d, J=8 Hz), 7.02 (1H, dd, J=13, 2.5 Hz), 7.03 (1H, br s), and 7.21 (1H, d, J=13 Hz). ^{13}C NMR δ=55.5, 55.8, 56.0, 65.8, 107.3, 111.4, 113.8 (2C), 116.5, 125.3, 132.5, 137.6, 150.6, 153.8, 158.8, 159.5, and 179.7. IR ν: 1566, 1507, 1220, 1200, and 1102 cm^{-1}. UV λ_{max}^{MeOH}: 227 nm (ε=31600), 252 (7600, sh), 310 (9600, sh), 328 (11300), 347 (9900), 362 (3900, sh), and 378 (6300, sh)].

Thermolysis of 16. Formation of 3-(2,5-Dimethoxybenzyl)-5-methoxytropolone (17). A decalin solution (5 cm^3) of **16** (128 mg) was refluxed under an N_2 atmosphere for 3 h. A silica-gel column chromatography of the mixture afforded **17** [pale yellow crystals, mp 101—103°C, 96.3 mg; 93%. Found: C, 67.69; H, 6.01%. ^{1}H NMR δ=3.66 (3H, s), 3.69 (3H, s), 3.73 (3H, s), 4.11 (2H, s), 6.72 (1H, dd, J=11, 3 Hz), 6.7—6.9 (3H, m), 7.09 (1H, d, J=3 Hz), and 7.26 (1H, d, J=11 Hz). ^{13}C NMR δ=34.9, 55.6 (2C), 55.9, 111.4, 112.0, 117.2, 117.7, 120.3, 122.9, 124.2, 140.7, 151.8, 153.5, 158.5, 162.8, and 170.6. IR ν: 1610, 1540, 1498, 1451, 1226, 1205, and 1055 cm^{-1}. UV λ_{max}^{MeOH}: 230 nm (ε=21500), 250 (16200, sh), 300 (5200), 341 (7800), 388 (5200), and 416 (2300, sh)] and **16** [23.9 mg; 19%].

Demethylation of 17. An AcOH solution (7.5 cm^3) of **17** (328 mg) and HBr (48%, 7.5 cm^3) was refluxed for 2 h. The mixture was then diluted with water and extracted with AcOEt. After evaporation of the solvent, the residue was recrystallized from $CHCl_3$ to give **18** [yellow crystals, mp 162—165°C (decomp), 276 mg; 93%. Found: M.W., 274.0856. Calcd for $C_{15}H_{14}O_5$: 274.0841. ^{1}H NMR (CD_3OD) δ=3.73 (3H, s), 4.02 (2H, s), 6.45—6.7 (3H, m), 6.92 (1H, dd, J=11, 3 Hz), 7.33 (1H, d, J=11 Hz), and 7.34 (1H, d, J=3 Hz). ^{13}C NMR (CD_3OD) δ=36.4, 56.4, 115.7, 117.7, 118.4, 119.3, 122.7, 127.6, 130.6, 144.1, 149.4, 151.5, 160.7, 163.9, and 172.4. IR ν: 3300—3100, 1618, 1504, 1452, 1398, and 1208 cm^{-1}. UV λ_{max}^{MeOH}: 228 nm (ε= 19600, sh), 249 (25400), 339 (11800), and 395 (9100)].

The DDQ-Oxidation of 18. To an acetone solution (9 cm^3) of **18** (93.2 mg), DDQ (85.6 mg) was added stirred at room temperature for 2 h. A brief silica-gel column chromatography of the mixture afforded **3** [deep yellow crystals, mp 105—107°C (decomp), 52 mg; 56%. Found: C, 65.78; H, 4.42%; M.W., 272.0682. Calcd for $C_{15}H_{12}O_5$: C, 66.17; H, 4.44%; M.W., 272.0682. ^{1}H NMR δ=3.79 (3H, s), 3.89 (2H, d, J=1.5 Hz), 6.52 (1H, dtd, J=2, 1.5, 1 Hz), 6.65 (1H, dd, J=10, 2 Hz), 6.77 (1H, dd, J=11, 3 Hz), 6.78 (1H, dd, J=10, 1 Hz), 7.46 (1H, d, J=11 Hz), and 7.47 (1H, d, J=3 Hz). ^{13}C NMR δ=34.9, 56.1, 118.4, 120.6, 130.7, 133.7, 136.6, 136.8, 137.2, 146.3, 158.8, 163.1, 171.0, 187.2, and 187.8. IR ν: 3600—3300, 1652, 1208, and 1200 cm^{-1}. UV $\lambda_{\max}^{\mathrm{MeOH}}$: 246 nm ($\varepsilon$=30800), 338 (11900), and 400 (7400)].

Electrolysis of 19 to 24. An anhydrous DMF solution (30 cm^3) of **19** (616 mg) was electrolyzed in the presence of TBAF (1 g) at −1.30 V for 22 h. After evaporation of the solvent in vacuo, the residue was diluted with AcOEt to precipitate **24** [258 mg; 44%], which was identical with the authentic sample.[9]

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