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Chemistry of 4,4-Dimethoxycyclohexa-2,5-dienone. Unusual Formation of Bridged Polycyclic Compounds

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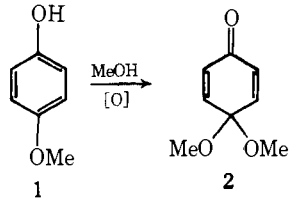
Abstract: Michael reactions of 4,4-dimethoxycyclohexa-2,5-dienone (**2**), readily available by electrochemical or chemical oxidation of *p*-methoxyphenol, were studied. Reaction of **2** with morpholine gave a mono-Michael adduct; methoxide gave a mixture of mono and bis adducts, and MeSH and PhSH gave only bis adducts. Reaction of **2** with Na_2S gave good yields of a novel polycyclic compound, decahydro-3,3,8,8-tetramethoxy-2,7-epithio-1,4-ethanonaphthalene-5,9-dione (**10**). Reaction of **10** with trimethyl orthoformate gave ketal **14** (decahydro-3,5,8,8,9,9-hexamethoxy-2,7-epithio-3,5-epoxy-1,4-ethanonaphthalene). Desulfurization and hydrolysis of **14** gave **16** (decahydro-1,4-ethanonaphthalene-2,5,8,10-tetraone), which is formally a Diels–Alder dimer of hydroquinone. Wolff–Kishner reduction of **16** gave the known hydrocarbon **17**, verifying the structures of **16** and **10**.

Introduction

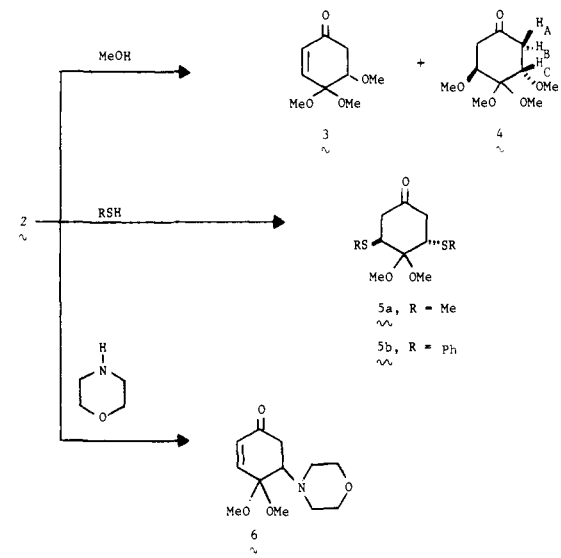
Several workers[1–3] have recently reported syntheses of 4,4-dimethoxycyclohexa-2,5-dienone (**2**), based on chemical



1 2

or electrochemical oxidation of *p*-methoxyphenol (**1**). Although this work has made **2** readily available, little work has focused on the chemistry of **2**.[4] We have prepared **2** by anodic oxidation of **1** in MeOH and have studied reactions of **2** with nucleophiles. The addition of LiOH to a methanolic solution of **2** caused spontaneous Michael addition of MeOH to give an equilibrium mixture of **2** (trace), **3** (83%), and **4** (17%) which was separable by gas chromatography (GC). The assignment of stereochemistry in **4** is based on the ^1H NMR spectrum which showed the -OMe absorptions of the ketal as equivalent. In addition, the absorptions of the ring protons (H_A, H_B, H_C) matched the computer-calculated spectrum (at both 60 and 100 MHz) for the trans isomer but not the cis isomer.

Scheme I



Attempts to produce pure **4** by refluxing the reaction mixture for 48 h failed to change the mixture.

Reaction of **2** with MeSH or PhSH gave only bis adducts

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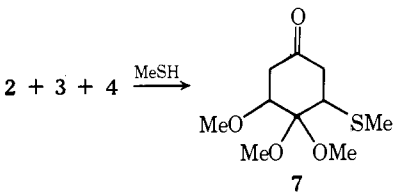
(**5a** and **5b**) in high yield. The stereochemistry in **5a** and **5b** was assigned as trans owing to the equivalence of the ketal -OMe protons in the ^{1}H NMR spectrum and by analogy with **4**. When **2** was dissolved in morpholine and heated briefly, the mono adduct **6** was formed and was the only product isolated.

Reaction of MeSH with the mixture of **2**, **3**, and **4** produced previously gave a white, crystalline solid (mp 67–69 °C) that appeared to be pure **7** by ^{1}H NMR but was shown by elemental



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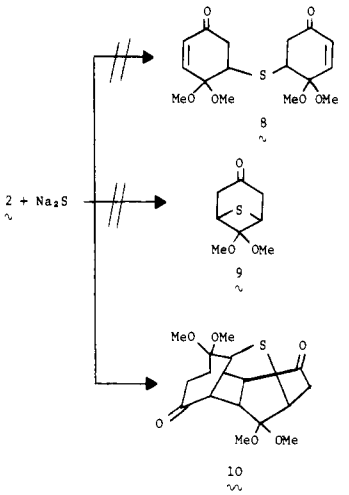
analysis and mass spectrometry to contain a trace of **5a**, which was not removed by recrystallization. A pure sample of **7** was never obtained. Since the presence of two different functionalities β to the carbonyl (-SMe and -OMe) in **7** necessitates nonequivalent ketal methyl groups in the ^{1}H NMR regardless of stereochemistry, the assignment of trans stereochemistry is based on analogy with **4** and **5**.

The facility with which **2** reacted with sulfur nucleophiles led us to attempt reaction of **2** with sulfide. Initially, we believed that this reaction would lead either to **8** or **9** or polymeric material (Scheme II). Reaction of **2** with aqueous Na_2S gave

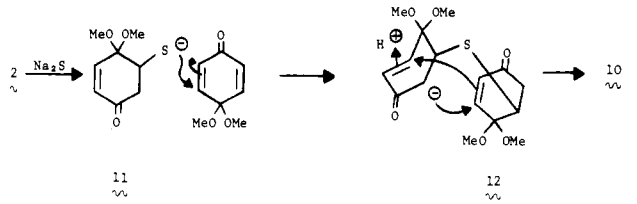
Scheme II



a solid product (mp 201–203 °C) which had spectral properties inconsistent with either **8** or **9**. The ^{1}H NMR spectrum showed no absorptions for vinyl protons and indicated at least three nonequivalent methyl groups, ruling out **8** or **9**. The infrared spectrum showed two carbonyl absorptions, also ruling out **8** or **9**, although the molecular weight (342, mass spectrum) and elemental analysis were consistent with structure **8**. Thus, it was apparent that the product was formally a combination of 2 mol of **2** and 1 mol of H_2S, but was not **8**. The actual structure, **10**, was arrived at by consideration of alternative reactions available to the Michael addition products, keeping in mind the requirement that the product possessed no vinyl protons. This led to the conclusion that intermediate **12** must not protonate immediately to give **8**, but must first undergo two intramolecular Michael additions as shown in Scheme III. The plausibility of this mechanism is easily seen by use of molecular models and by noting that each ring closure forms a new six-membered ring.

In addition, it was discovered that **10** is apparently the thermodynamically favored product in the various equilibria involved in Michael addition of sulfide to **2** since reaction of Na_2S with the mixture of **2**, **3** and **4** (predominantly **3**) gave

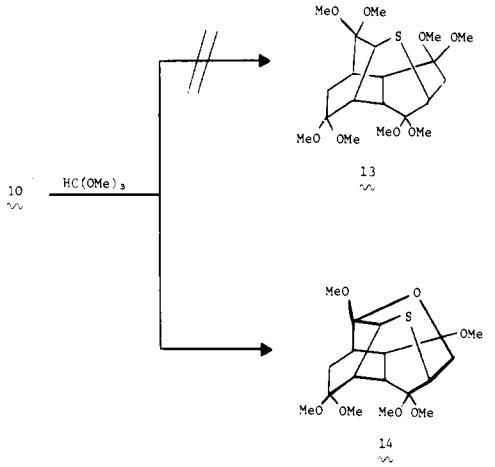
Scheme III



10 in ~60% yield (42% yield was obtained from pure **2**). The mechanism of this reaction must involve at some stage a reverse-Michael addition of methoxide.

To our knowledge, structure **10** is a novel ring system, and therefore merits further study of its chemistry. This consideration, and a desire for further structure proof, led us to attempt desulfurization of **10** to a known ring system. However, attempts to desulfurize **10** with Raney nickel in a variety of solvents led to mixtures of products, some of which had been reduced at the carbonyls. To avoid this complication, the ketones were first converted to methyl ketals by reaction with trimethyl orthoformate (Scheme IV). A crystalline product

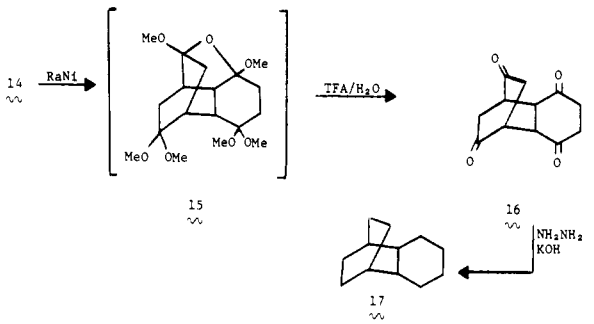
Scheme IV



possessing no carbonyls (infrared) was obtained, but the mass spectrum and elemental analysis indicated that it had two methyls and one oxygen less than expected product **13**. This is easily reconciled by formation of one cyclic ketal to give structure **14**. Alternative structures produced by forming a cyclic ketal between any two ketals in **13** cannot be rigorously ruled out, but inspection of molecular models indicates that **14** is the most likely structure. The exact position of the cyclic ketal has no effect on further conversions of **14**.

Desulfurization of **14** gave an oil, presumably **15** (Scheme V), which was not purified, but was hydrolyzed with trifluo-

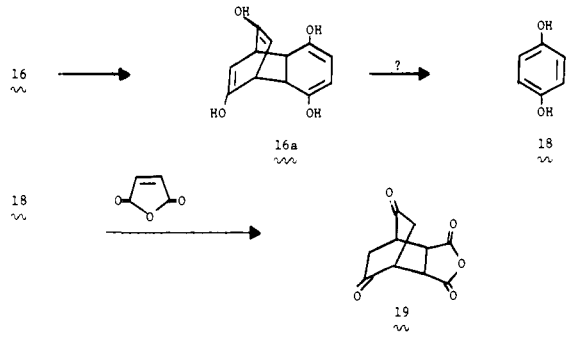
Scheme V



roacetic acid (TFA) in water to give tetraketone **16**. Reduction of **16** gave the known tricyclododecane **17**,[5] providing additional proof of structures **10** and **16**.

Tetraketone **16** is of further interest because it is formally a Diels–Alder dimer of hydroquinone (Scheme VI), as shown

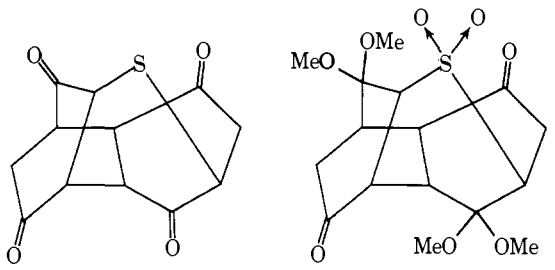
Scheme VI



by inspection of its tautomer **16a**. Indeed a major fragmentation in the mass spectrum (*m/e* 110) can be explained by reverse Diels–Alder to give hydroquinone. Attempts to convert **16** to **18** by pyrolysis were inconclusive as only small amounts of products were isolated. In one attempt TLC and GC evidence did indicate the presence of **18**.

In studying this formal Diels–Alder adduct of hydroquinone, we found three previous reports of the Diels–Alder reaction of hydroquinone with maleic anhydride to give adduct **19**[6-8] in low yield. We have repeated this reaction and found that ^{1}H NMR spectra of **19** and **16** are very similar (see Experimental Section) as predicted.

Further work on the chemistry of **10** has included hydrolysis to tetraketone **20** and oxidation to sulfone **21**.



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Experimental Section

General. Melting points are uncorrected. Infrared spectra were recorded using a Perkin-Elmer Model 137 or Model 621; ^{1}H NMR spectra were recorded on a Varian EM-360 (60 MHz), Jeolco MH-100 (100 MHz), or a Perkin-Elmer R-32 (90 MHz). ^{13}C NMR spectra were determined with a Bruker HX-90E (22.628 MHz). Calculation of ^{1}H NMR spectra for **4** was done using a Nicolet NIC-80/S-7117-D computer program. All NMR chemical shift data are reported in parts per million (ppm) downfield from Me_4Si (internal). Mass spectra were recorded with a Consolidated Electrodynamics Corp. Model 21-110B or Finnigan Instruments Corp. Model 1015S/L instrument. GC analyses were done using a 6 ft × 0.25 in. stainless steel column using 5% Apiezon L liquid phase on 60–80 mesh Chromosorb G packing (DMCS treated, acid washed).

4,4-Dimethoxycyclohexa-2,5-dienone (2). The procedure of Nilsson et al.[1] was generally followed. *p*-Methoxyphenol (20 g) dissolved in methanol (120 mL) containing lithium perchlorate (8 g) was stirred magnetically and subjected to constant current (2.0 A) electrolysis at a cell voltage of about 25 V on a platinum anode (50 cm^2) in an open water-cooled (10 °C) vessel. The cathode was a 6-cm length of copper wire[9] (diameter 0.7 mm). The oxidation was monitored by NMR or GC. When 95–100% of the starting material had been consumed (this requires about 3.6 faradays/mol, corresponding to an electrolysis time of about 8 h), the electrolysis mixture was poured into a phosphate buffer (pH 6, 600 mL). Extraction with dichloromethane (3 × 150 mL) followed by evaporation at reduced pressure (the temperature of the heating bath should not exceed 30 °C) gave crude **2** (24 g).[10] Further purification can be achieved by filtration through neutral alumina (Woelm Dry Column, activity III, ethyl acetate eluent) or by distillation at reduced pressure, but decomposition of the dienone reduces the yield substantially on distillation.

3,4,4-Trimethoxycyclohex-5-enone (3) and *trans*-3,4,4,5-Tetramethoxycyclohexanone (4). To a solution of **2** (1.0 g) in MeOH (5 mL) was added $LiOH\cdot H_2O$ (0.04 g). The mixture darkened immediately. After stirring for 2 h at room temperature, water and CH_2Cl_2 were added, and the CH_2Cl_2 layer was evaporated to give a yellow oil, shown by VPC analysis to be three components: **2** (trace) and **3**, and **4** (≈5/1). Essentially the same mixture was obtained when preparation of **2** was attempted using a platinum cathode in the presence of a small amount of LiOH. The mixture was not separated on distillation through a 6-in. Vigreux column (94–97 °C, 1.2 Torr), but was separated by preparative GC to give **3** as a colorless liquid: IR (KBr) 1680, 1110, 1095, 1045, 950 cm^{-1}; ^{1}H NMR (acetone-d_6) δ 6.90 (dd, J_1 = 2, J_2 = 11 Hz, 1 H), 6.07 (d, J = 11 Hz, 1 H), 4.0 (m, 1 H), 3.45 (s, 3 H), 3.40 (s, 6 H), 2.80 (d, J = 3 Hz, 2 H); mass spectrum *m/e* 171 (M − 15), 128, 113, 99, 95, 59, 55.

Anal. Calcd for $C_9H_{14}O_4$: C, 58.05; H, 7.58. Found: C, 58.08; H, 7.59.

The minor component, **4**, was also isolated by preparative GC as a colorless liquid: IR (neat) 2898, 2816, 1709, 1086 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.80 (m, 2 H), 3.48 (m, 12 H), 2.68 (m, 4 H); ^{1}H NMR (calculated) used J_{AB} = 18.0, J_{AC} = 7.0, J_{BC} = 1.0 Hz; mass spectrum *m/e* 203 (M − 15), 131, 117, 101, 75, 55.

***trans*-3,5-Bis(methylthio)-4,4-dimethoxycyclohexanone (5a).** To a solution of **2** (2.0 g, 13 mmol) in 20 mL of CH_3SH at 0 °C was added $LiOH\cdot H_2O$ (0.04 g). The mixture was stirred for 1 h at 0 °C under N_2, then CH_3SH was allowed to evaporate into a NaOH/NaOCl trap. The residue was dissolved in CH_2Cl_2, washed with H_2O, dried over Na_2SO_4, and evaporated to give **5a** as a white solid (3.2 g, 100% yield) which after recrystallization from CH_2Cl_2/hexane melted at 73–76 °C: IR (KBr) 2898, 1715, 1124, 1099, 1071, 1052, 1029, 924 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.52 (s, 6 H), 3.48 (m, 2 H), 2.80 (m, 4 H), 2.20 (s, 6 H); mass spectrum *m/e* 250 (M), 147, 101, 55.

Anal. Calcd for $C_{10}H_{18}O_3S_2$: C, 47.97; H, 7.25; S, 25.61. Found: C, 47.83; H, 6.98; S, 25.38.

***trans*-3,4,4-Trimethoxy-5-methylthiocyclohexanone (7).** The distilled mixture of **2**, **3**, and **4** obtained previously (3.0 g) was treated with 15 mL of CH_3SH and 50 mg of $LiOH\cdot H_2O$ (as shown previously) to give 3.5 g of white solid (**7**) which melted at 67–69 °C after recrystallization from $EtOH/H_2O$: IR (KBr) 2941, 1718, 1130, 1099, 1079, 1058, 1034, 928 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.86 (m, 1 H), 3.48 (m, 10 H), 2.72 (m, 4 H), 2.20 (s, 3 H); mass spectrum *m/e* 250 (**5a**), 234 (M), 147, 117, 101, 55.

Elemental analysis of this product gave high values for S, indicating that a pure sample was not obtained, even after repeated recrystallizations.

***trans*-3,5-Bis(phenylthio)-4,4-dimethoxycyclohexanone (5b).** To a stirred solution of **2** (1.0 g) in thiophenol (~15 mL) under N_2 was added $LiOH\cdot H_2O$ (0.1 g) at room temperature; stirring was continued for 30 min. Excess thiophenol was removed by distillation at room temperature (0.1 Torr). CH_2Cl_2 and H_2O were added to the residue. The layers were separated and the CH_2Cl_2 layer was dried (Na_2SO_4) and evaporated to give 2.4 g (99% yield) of white solid **5b** (pure by NMR). Recrystallization from 95% EtOH gave 1.9 g of **5b**: mp 103–105 °C; IR (KBr) 2941, 1709, 1585, 1479, 1435, 1206, 1190, 1139, 1121, 1092, 1075, 1055, 1022, 927, 746, 692 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.7–7.25 (m, 10 H), 4.04 (dd, J_1 = 6, J_2 = 8 Hz, 2 H), 3.64 (s, 6 H), 2.78 (m, 4 H); mass spectrum *m/e* 374 (M), 209, 109, 101, 65, 55.

Anal. Calcd for $C_{20}H_{22}S_2O_3$: C, 64.14; H, 5.92; S, 17.12. Found: C, 64.39; H, 5.97; S, 17.17.

4,4-Dimethoxy-3-morpholinocyclohex-5-enone (6). A solution of **2** (1 g) in 6 g of morpholine was stirred at 80 °C for 5 h. Excess morpholine was removed under vacuum to give an oil. Trituration with hexane gave a white solid (1.0 g, 64% yield). An analytical sample was obtained by recrystallization from hexane: mp 84–86 °C; IR (KBr) 2933, 2825, 2801, 1678, 1259, 1118, 1048, 967 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.72 (d, J = 11 Hz, 1 H), 6.02 (d, J = 11 Hz, 1 H), 3.62 (t, J = 4.5 Hz, 4 H), 3.4 (s, 3 H), 3.37 (s, 3 H), 3.26 (m, 1 H), 2.56–3.0 (m, 4 H), 2.28–2.55 (m, 2 H); mass spectrum *m/e* 241 (M), 128, 59, 56, 55.

Anal. Calcd for $C_{12}H_{19}NO_4$: C, 59.73; H, 7.93; N, 5.80. Found: C, 60.00; H, 7.74; N, 5.64.

Decahydro-3,3,8,8-tetramethoxy-2,7-epithio-1,4-ethanonaphthalene-5,9-dione (10). A. A solution of $Na_2S\cdot 9H_2O$ (4.8 g, 0.02 mol) in H_2O (10 mL) was added to a stirred mixture of **2** (3 g, 0.02 mol) and H_2O (40 mL) at 10 °C. The mixture was stirred at 10 °C for 2

h. The ice bath was removed and stirring was continued at room temperature for 48 h. The product, **10**, precipitated and was isolated by filtration, washed with H_2O, and dried (1.44 g, 42% yield). Recrystallization from EtOH gave a sample which melted at 201–205 °C, but on solidification and remelting gave mp 201–203 °C. The infrared spectra of the initial and melted samples were identical: IR (KBr) 1727, 1700, 1111, 1064, 1046 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.28 (s, 3 H), 3.24 (s, 6 H), 3.16 (s, 3 H), 3.14–1.9 (m, 10 H); ^{13}C NMR ($CDCl_3$) 209.5, 208.4, 101.0, 97.1, 51.1, 49.7, 48.4, 48.3, 47.6, 46.1, 44.7, 42.4, 40.7, 39.4, 36.7, 31.9 ppm; mass spectrum *m/e* 342 (M), 101, 91, 75, 59, 55.

Anal. Calcd for $C_{16}H_{22}O_6S$: C, 56.12; H, 6.48; S, 9.37. Found: C, 56.34; H, 6.40; S, 9.33.

B. A solution of Na_2S (fused chips, ~60%, 0.01 mol) in H_2O (10 mL) was added to a stirred mixture of 20 mL of H_2O and 1.86 g (~0.01 mol) of the product (**3** and **4**) of treatment of **2** with LiOH/MeOH (as shown previously). After stirring for 24 h at room temperature **10** was isolated by filtration. The yield was 1.05 g, or 61% based on 1.86 g of **3**.

Decahydro-2,7-epithio-1,4-ethanonaphthalene-3,5,8,9-tetraone (20). A solution of ketal **10** (0.5 g) in 20 mL of trifluoroacetic acid (TFA)/H_2O (9/1) was stirred at room temperature for 2 h. Evaporation of volatiles under vacuum gave a brown solid which gave **20** as a white solid on trituration with acetone, recrystallization (acetone), or sublimation (0.05 Torr, 180 °C): mp 204–219 °C dec; IR (Nujol) 1709 (broad), 1157 cm^{-1}; ^1H NMR (TFA) δ 4.2–3.9 (m, 2 H), 3.9–3.56 (m, 6 H), 3.14 (m, 2 H); mass spectrum *m/e* 250 (M), 222, 134, 100, 95, 94.

Anal. Calcd for $C_{12}H_{10}SO_4$: C, 57.58; H, 4.02; S, 12.81. Found: C, 57.29; H, 4.17; S, 12.62.

Decahydro-3,5,8,8,9,9-hexamethoxy-2,7-epithio-3,5-epoxy-1,4-ethanonaphthalene (14). A mixture of trimethyl orthoformate (5.3 g, 0.05 mol), **10** (3.42 g, 0.01 mol), *p*-toluenesulfonic acid (0.25 g), and MeOH (100 mL) was refluxed for 4 h. After cooling to room temperature, aqueous $NaHCO_3$ was added to cause precipitation of **14** as an off-white solid, isolated by filtration (3.0 g, 77% yield). An analytical sample (mp 175–179 °C) was prepared by sublimation (140 °C, 0.04 Torr): IR (KBr) 2941, 1148, 1111, 1055, 1045, 961 cm^{-1}; NMR ($CDCl_3$) δ 3.44 (s, 3 H), 3.38 (s, 3 H), 3.24 (m, 12 H), 2.28–3.08 (m, 8 H), 1.8 (d, J = 3 Hz, 2 H); mass spectrum *m/e* 388 (M), 357, 159, 105, 101, 75.

Anal. Calcd for $C_{18}H_{28}SO_7$: C, 55.65, H, 7.26; S, 8.26. Found: C, 55.63; H, 7.03; S, 8.39.

Desulfurization of 14. A mixture of Raney nickel (4.0 g), **14** (4.0 g), and *p*-xylene (125 mL) was refluxed for 6 h. Filtration (Celite) and evaporation of xylene gave 4.0 g of brown oil which was used directly in preparation of **16**. (See the following.)

Decahydro-1,4-ethanonaphthalene-2,5,8,10-tetraone (16). The brown oil (4.0 g) obtained from desulfurization of **14** was dissolved in 50 mL of TFA/H_2O (9/1). Evaporation of TFA/H_2O under vacuum gave a brown gum which gave a white solid (mp 203–207 °C, 400 mg) on trituration with acetone. Sublimation (200 °C, 0.05 Torr) or recrystallization from acetone did not change the melting point: IR (KBr) 1709 (broad), 1393, 1248, 1082, 938 cm^{-1}; ^1H NMR ($CDCl_3$/Me_2SO-d_6) δ 3.87 (dd, J_1 = 3, J_2 = 12 Hz, 1 H), 3.65 (dd, J_1 = 3, J_2=12 Hz, 1 H), 3.15 (m, 4 H), 2.37–2.73 (m, 6 H); mass spectrum *m/e* 220 (M), 110, 79, 55.

Anal. Calcd for $C_{12}H_{12}O_4$: C, 65.44; H, 5.49. Found: C, 65.67; H, 5.71.

Decahydro-1,4-ethanonaphthalene (17). A mixture of **16** (110 mg), 95% hydrazine (550 mg), KOH (350 mg), and triethylene glycol (5 mL) was refluxed for 45 min. The condenser was removed to distill off NH_2NH_2/H_2O and the bath temperature was raised to 205–210 °C. The condenser was replaced and heating continued for 3 h. The mixture was extracted with hexane. GC and infrared analysis of the hexane extract indicated that the product was identical with **17** prepared by known methods.[5]

Hydroquinone–Maleic Anhydride Adduct, 19 (Bicyclo[2.2.2]octane-2,5-dioxo-7,8-dicarboxylic Anhydride). Using a known procedure[6,7] **19** was obtained as white crystals (recrystallized from acetone/acetic anhydride): mp 270–272 °C dec; IR (KBr) 1869, 1782, 1724, 1232, 1098, 1086, 926 cm^{-1}; ^1H NMR ($CDCl_3$/Me_2SO-d_6) δ 4.04 (dd, J_1 = 3, J_2 = 12 Hz, 1 H), 3.84 (dd, J_1 = 3, J_2 = 12 Hz, 1 H), 3.2 (m, 2 H), 2.74 (m, 2 H), 2.54 (m, 2 H); mass spectrum *m/e* 208 (M), 94, 79, 66.

Attempted Pyrolysis of 16. A. Heating **16** in a sublimation apparatus at 275 °C (20 Torr) gave a black tar and a small amount of white sublimate, identified as **16** by infrared.

B. A solution of **16** (100 mg) in acetone (10 mL) was dropped through a tube packed with Vycor chips heated at 260 °C or at 355 °C. TLC (silica gel, 50% hexane/acetone) and GC analysis indicated the presence of small amounts of hydroquinone.

Decahydro-3,3,8,8-tetramethoxy-2,7-epithio-1,4-ethanonaphthalene-5,9-dione *S,S*-Dioxide (21). A solution of sulfide **10** (684 mg, 2 mmol) in $CHCl_3$ (5 mL) was added to a solution of *m*-chloroperbenzoic acid (MCPBA, Aldrich, 812 mg, 4 mmol) in 7 mL of $CHCl_3$. The solution was stirred at ambient temperature (an initial exotherm occurred) for 4.5 h. The mixture was diluted with 10 mL of $CHCl_3$ and washed with aqueous K_2CO_3. The $CHCl_3$ layer was dried (Na_2SO_4) and evaporated to give a white solid, **21** (720 mg, 96% yield). An analytical sample was prepared by recrystallization from acetone/hexane: mp 265–266 °C dec (gas evolution); IR (KBr) 1730, 1709, 1314, 1107, 1049, cm^1; NMR ($CDCl_3$) δ 3.7–2.0 (m), $-OCH_3$ singlets at 3.40, 3.30, 3.27, 3.09; mass spectrum *m/e* 374 (M), 278, 128, 101, 59, 55.

Anal. Calcd for $C_{16}H_{22}SO_8$: C, 51.32; H, 5.92; S, 8.56. Found: C, 51.59; H, 5.95; S, 8.76.

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References and Notes

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(9) Nilsson et al.[1] used a tungsten wire but copper is more readily available. Pt is not acceptable for the cathode.
(10) The yield of the reaction is determined mainly by the acid-catalyzed hydrolysis of the ketal to give *p*-benzoquinone. In high humidity, the yield of **2** can be improved by more carefully excluding water.