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Mixed Methyl Silyl Ketals of Quinones: Their Preparation via Anodic Oxidation and Their Chemistry

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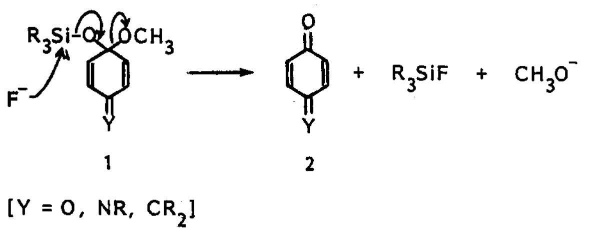
Anodic oxidation of *tert*-butyldimethylsilyl and *tert*-butyldiphenylsilyl derivatives of *p*-methoxyphenols affords quinone bisketals containing the uncommon alkyl silyl ketal unit. Acid hydrolysis of these quinone bisketals affords monoketals derived from hydrolysis of the dimethyl ketal unit: the alkyl silyl ketal units are more stable toward acid hydrolysis. These same monoketals can be prepared from anodic oxidation of *tert*-butyldimethylsilyl and *tert*-butyldiphenylsilyl monoethers of hydroquinone. The mixed alkyl silyl ketals above are deblocked rapidly to the carbonyl derivative with tetrabutylammonium fluoride in tetrahydrofuran.

Introduction

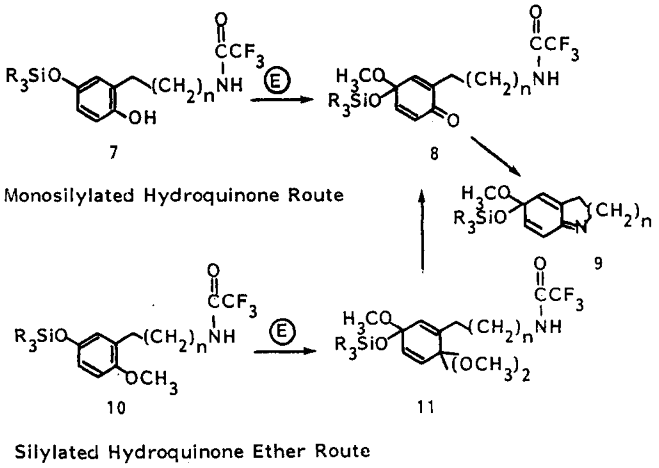
Quinone bisketals are protected quinone derivatives[1] which are readily converted to synthetically versatile quinone monoketals[2] by acid hydrolysis. However, for preparation of highly reactive and/or acid-labile quinone derivatives (e.g., quinone imines[3]), a carbonyl protecting group which could be deblocked under mild, neutral conditions in nonnucleophilic media is desirable (Scheme I). One candidate for such a carbonyl blocking group is the mixed alkyl silyl ketal such as 1 which should react with a fluoride ion source under mild conditions to generate the carbonyl group, trialkylsilyl fluoride, and alkoxide ion. Such mixed alkyl silyl ketals are reported only rarely in the literature,[4] and little information is available on their synthesis or stability.

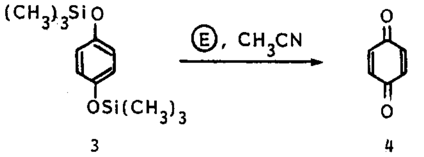
Scheme I. Strategy for Nonoxidative Generation of Quinone Derivatives from Alkyl Silyl Ketals

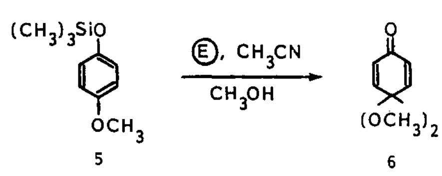


Two known routes to quinone imine ketals[5] could be adapted (Scheme II) to generate the biologically interesting quinone imine if silylated aromatic ethers underwent anodic oxidation with retention of the silyl ether linkage. However, the reported anodic oxidations of silyl ethers of phenols always involved loss of the silyl ether moiety.[6] Electrochemical oxidation of bis(trimethylsilyl ethers) of various hydroquinones in acetonitrile or methylene chloride solution afforded the corresponding quinone in excellent yields (3 → 4). Even when the anodic oxidation was conducted in methanol–acetonitrile, the trimethylsilyl derivative of *p*-methoxyphenol gave the desilylated product 6 in quantitative yield (5 → 6). Interestingly, cyclic voltammetric studies have established that the silicon–oxygen bond was cleaved at the radical cation stage of the oxidation and that the rate of silicon–oxygen cleavage was in the order 10:5:1 for the trimethylsilyl, triethylsilyl, and *tert*-butyldimethylsilyl groups.[6] Thus, despite the facile cleavage of the silyl group in preparative anodic oxidation studies, the cyclic voltammetric results suggested the possibility of preparing mixed alkyl silyl ketals by anodic oxidation of appropriate aromatic ether derivatives if close attention were paid to substrate and reaction conditions.

Scheme II. Projected Routes to Mixed Quinone Imine Ketals







We report herein (1) the anodic oxidation of silylated derivatives of *p*-methoxyphenols and the monosilylated derivatives of hydroquinones to yield mixed methyl silyl ketals as oxidation products, (2) some of the limitations of these oxidations, (3) acid-catalyzed hydrolysis of quinone bisketals derived from above, and (4) fluoride ion deblocking of the mixed alkyl silyl ketal moiety.

Results and Discussion

Anodic Oxidation of Monosilylated Hydroquinones. The two routes outlined in Scheme II would furnish mixed

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[1] (a) Henton, D. R.; McCreery, R. L.; Swenton, J. S. *J. Org. Chem.* **1980**, *45*, 369. (b) For a review of quinone bisketal and monoketal chemistry, see: Swenton, J. S. *Acc. Chem. Res.* **1983**, *16*, 74.

[2] Henton, D. R.; Anderson, D. K.; Manning, M. J.; Swenton, J. S. *J. Org. Chem.* **1980**, *45*, 3422.

[3] (a) For a review of the older literature on quinone imines, see: Patai, S. *The Chemistry of the Carbon–Nitrogen Double Bond*; Interscience: New York, 1970; pp 633–729. (b) Brown, K. C.; Corbett, J. F. *J. Chem. Soc., Perkin Trans. 2* **1981**, 886 and earlier papers in the series. (c) Nogami, T.; Hishida, T.; Yamada, M.; Mikawa, H.; Shirota, Y. *Bull Chem. Soc. Jpn.* **1975**, *48*, 3709. (d) Harmalker, S. P.; Sawyer, D. T. *J. Org. Chem.* **1984**, *49*, 3579 and references cited therein. (e) Young, T. E.; Beidler, W. T. *J. Org. Chem.* **1984**, *49*, 4833. (f) Young, T. E.; Babbitt, B. W. *J. Org. Chem.* **1983**, *48*, 562 and references cited therein.

[4] Nakai, N. *Chem. Lett.* **1986**, *8*, 1355.

[5] Chen, C.; Shih, C.; Swenton, J. S. *Tetrahedron Lett.* **1986**, *27*, 1891.

[6] Stewart, R. F.; Miller, L. L. *J. Am. Chem. Soc.* **1980**, *102*, 4999.

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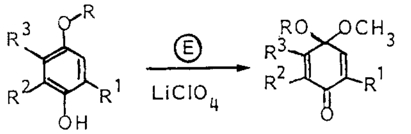
quinone monoketals which could be subsequently converted to quinone imines. The monosilylated hydroquinone route requires anodic addition to afford compounds analogous to **8**. The second approach, **10** → **11** → **8**, requires not only a 1,4-anodic addition with retention of the silyl group to give **11** but also selective hydrolysis of the dimethyl ketal of **11**. Before implementing the strategies of Schemes I and II, it was necessary to establish conditions for the unknown chemical transformations embodied in these proposals.

We began by examining preparative oxidations of monosilylated derivatives of hydroquinone[7] since these oxidations can be conducted in the absence of methoxide or hydroxide ion, conditions which would favor retention of the silyl ether linkage. Since cyclic voltammetric studies[6] had indicated that more substituted silyl groups underwent slower cleavage, the anodic oxidation of the *tert*-butyldimethylsilyl derivative of hydroquinone was the first compound studied. Anodic oxidation of **12a** in a single cell at −10 °C using 2% lithium perchlorate in methanol as the electrolyte–solvent system, followed by standard workup and chromatography on neutral alumina, afforded **13a** (58%) as a clear oil. The compound showed analytical and spectroscopic data in agreement with **13a**, the most diagnostic being the signals for the *tert*-butyldimethylsilyl group at δ 0.88 (s, 9 H) and 0.11 (6 H). A comparable yield of the mixed quinone monoketal was obtained when the *tert*-butyldiphenylsilyl-protected phenol **12b** was anodically oxidized under similar conditions. Two other compounds, **12c**,**d**, gave similar results. No other products were characterized from these reactions; therefore, it is not possible to suggest reasons for yields of 53–77%. These reactions provide the first examples in which the silyl ether linkage of a phenol is retained in the anodic oxidation reaction in preparatively useful yield.

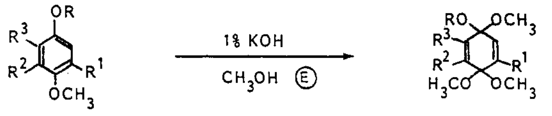


12 13

	R	R^1	R^2	R^3	
12a	Si-*t*-Bu$(CH_3)_2$	H	H	H	**13a** (58%)
b	Si-*t*-BuPh_2	H	H	H	**b** (60%)
c	Si-*t*-BuPh_2	CH_3	H	H	**c** (53%)
d	Si-*t*-BuPh_2	CH_3	CH_3	CH_3	**d** (77%)

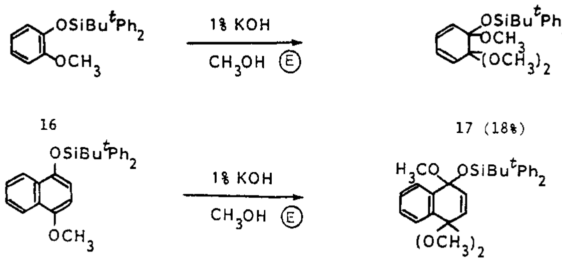
Anodic Oxidation of Silylated Methoxyphenols. The second approach to alkyl silyl quinone monoketals (Scheme II) requires anodic 1,4-addition of methanol to a silylated *p*-methoxyphenol derivative. Thus, the anodic oxidation of readily available **14a** was studied under constant-current conditions at a platinum anode in a single cell by using 1% methanolic potassium hydroxide as electrolyte–solvent at −15 °C (Scheme III). Monitoring the progress of the reaction by ultraviolet analysis showed disappearance of the aromatic absorption with the development of isosbestic points at 264 and 239 nm. Standard workup of the reaction mixture followed by chromatography on neutral alumina gave the mixed quinone bisketal **15a** (52%). The structure of the product was based on spectroscopic data: ^{1}H NMR [δ 5.95 (s, 4 H), 3.26 (s, 6 H), 3.21 (s, 3 H), 0.83 (s, 9 H), 0.08 (s, 6 H)], IR, and exact mass analysis. For the first time an anodic oxidation of an aromatic silyl ether had been conducted without complete loss of the silyl group.

Scheme III. Anodic Oxidations of Methoxy Siloxy-Substituted Aromatics



14 15

Entry	Compd	R	R^1	R^2	R^3	%
1	14a	$SiBu^t(CH_3)_2$	H	H	H	52
2	14b	$SiBu^tPh_2$	H	H	H	96
3	14c	$SiBu^tPh_2$	CH_3	H	H	92
4	14d	$SiBu^tPh_2$	CH_3	CH_3	CH_3	78
5	14e	$SiBu^tPh_2$	H	H	$CH(OCH_3)_2$	70
6	14f	$SiBu^tPh_2$	Br	H	H	0
7	14g	$SiBu^tPh_2$	OCH_3	H	H	0



8 16 17 (18%)

9 18 R = H 19 (72%)

Since the ultraviolet analysis of the **14a** reaction mixture showed two isosbestic points, the modest isolated yield (52%) of **15a** suggested that some of the product decomposed during the isolation. The 96% yield obtained from anodic oxidation of the *tert*-butyldiphenylsilyl derivative **14b** supports this idea since the *tert*-butyldiphenylsilyl linkage would be more stable to desilylation than the corresponding *tert*-butyldimethylsilyl derivative. Scheme III shows that unsubstituted and alkyl-substituted 4-methoxyphenols undergo oxidation to the mixed bisketals in good yields (entries 1–5). Only one naphthalene derivative was oxidized to the mixed bisketal (entry 9); this suggests that no inherent limitation exists when applying this chemistry to naphthalene systems. The *o*-methoxy compound **16** afforded a low yield of the mixed bisketal (entry 8), but this is not suprising since 1,2-dimethoxybenzene itself[8] gives the bisketal of *o*-benzoquinone in low yield.

The major limitation for successful oxidation of the *tert*-butyldiphenylsilyl ethers in these systems is not related to the electrochemical step but instead to the stability of the starting silyl derivatives in 1% methanolic potassium hydroxide. The qualitative stability of the silyl derivatives **14a**,**b**,**e**–**g**, **16**, and **18** was determined as follows. Solutions of the silylated phenols in ca. 1:5 tetrahydrofuran/1% methanolic potassium hydroxide at room temperature were monitored by TLC for desilylation to the corresponding

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[7] Anodic oxidation of *p*-methoxyphenols serves as an excellent route to quinone monoketals. (a) Nilsson, A.; Palmquist, U.; Pettersson, T.; Ronlán, A. *J. Chem. Soc., Perkin Trans. 1* **1978**, 696. (b) Foster, C. H.; Payne, D. A. *J. Am. Chem. Soc.* **1978**, *100*, 2834. (c) Chen, C.-P.; Swenton, J. S. *J. Chem. Soc., Chem. Commun.* **1986**, 1291. (d) Shizuri, Y.; Nakamura, K.; Yamamura, S.; Ohba, S.; Yamashita, H.; Saito, Y. *Tetrahedron Lett.* **1986**, *27*, 727.

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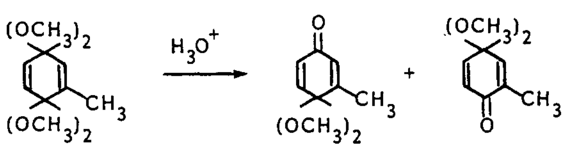
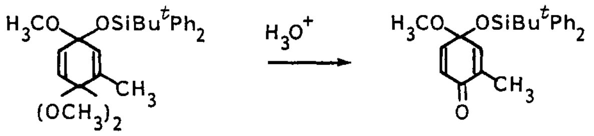
phenol. The silyl ethers **14f,g** substituted with the bromo and methoxy groups rapidly desilylated to their respective phenols, while the remaining compounds were much more stable under these conditions. Thus, oxidation of compounds **14f,g** could not be studied since desilylation occurs in the electrolysis solvent system. Apparently, the stability of the silyl derivatives in 1% methanolic potassium hydroxide is a function of the character of the substitutent on the aromatic ring. The higher electronegativity[9] of the methoxy (σ_I 0.27) and bromo (σ_I 0.44) groups relative to alkyl ($\sigma_I \sim -0.04$) or hydrogen (σ_I 0.00) substituents would favor desilylation occurring by nucleophilic attack of hydroxide or methoxide. However, the importance of this remote inductive effect is surprising.

Hydrolysis of Alkyl Silyl Ketals. The formation of mixed alkyl silyl bisketals by anodic oxidation of *p*-methoxy siloxy aromatics was established (Scheme III); however, there still remained the question of the regiochemistry of quinone bisketal monohydrolysis. To utilize the synthetic approach outlined in Scheme II the dimethyl ketal would be required to hydrolyze faster than the alkyl silyl ketal. Additionally, it was known that an alkyl substituent such as methyl favored hydrolysis of the more distant ketal in bis(dimethyl ketals) of benzoquinone; for example, **20** gives a 65:11 ratio of **21** and **22**.[2] Both of these points could be answered by examining the hydrolysis of **15c**. Hydrolysis of **15c** in aqueous acetic acid/acetone afforded the monoketal **13c** (89%). Thus, not only does the dimethyl ketal of **15c** hydrolyze faster than the alkyl silyl ketal but also the difference in rate of hydrolysis is sufficient to override the directive effect of the vinyl methyl group.[10-12]

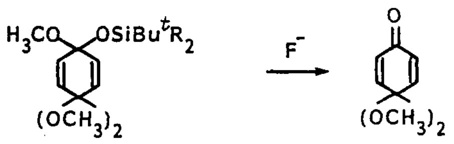


20 21 (65%) 22 (11%)



15c 13c (89%)

Desilylation of the Alkyl Silyl Ketals by Fluoride Ion. The final aspect of the chemistry is the deprotection of the alkyl silyl group to generate the carbonyl group under nonacidic conditions in the absence of nucleophiles. Such deblocking would be required for generation of highly reactive quinone imines, quinone methides, and quinones (Scheme I). Indeed, desilylation of **15a,b** in tetrahydrofuran solution occurs at 0 °C within minutes to afford the benzoquinone monoketal in yields of 76% and 80%, respectively.



15a, R = CH_3
b, R = Ph

Summary. Anodic oxidation of silylated *p*-methoxyphenols and monosilylated hydroquinones can be employed to prepare quinone bisketals and quinone monoketals containing the mixed alkyl silyl ketal unit. A limitation of the anodic oxidation is the desilylation of the starting compound under the reaction conditions. Interestingly, the mixed methyl *tert*-butyldimethylsilyl and methyl *tert*-butyldiphenylsilyl moieties are more stable under acid hydrolysis conditions than the dimethyl ketal unit. However, the alkyl silyl ketal unit is deblocked to the carbonyl group with tetrabutylammonium fluoride in tetrahydrofuran at 0 °C, establishing its viability for generation of highly reactive quinone derivatives under mild, nonacidic conditions. Such alkyl silyl ketals would be useful protecting groups for the simple carbonyl moiety if a direct method of preparing these compounds were available.

Experimental Section[13]

Preparation of Monosilylated Hydroquinones. 12a. *tert*-Butyldimethylsilyl chloride (1.3 g, 8.6 mmol) dissolved in dry acetonitrile (10 mL) was added dropwise over 5 min to a stirred solution of hydroquinone (0.9 g, 8.2 mmol) and imidazole (1.2 g, 17.6 mmol) in dry acetonitrile (10 mL) at 25 °C. At the end of the addition period the solution stayed clear for a short time and then a white solid precipitated. The acetonitrile was removed under reduced pressure, the residue was partitioned between Et_2O and water, and the organic phase was washed with 2% aqueous $NaHCO_3$ (25 mL). Silica gel chromatography (10 × 3 cm column, 10% EtOAc/PE as eluant) afforded **12a** (0.668 g, 36%) as a yellowish oil. Recrystallization from PE at −78 °C gave a white solid: mp 55.5–57 °C; IR (KBr) 1505 (s), 1228 (s), 835 (s), 822 cm^{-1} (s); ^1H NMR δ 6.68 (s, 4 H), 4.42 (br s, 1 H), 0.95 (s, 9 H), 0.14 (s, 6 H); mass spectrum, exact mass for $C_{12}H_{20}O_2Si$ calcd *m/e* 224.1232, obsd *m/e* 224.1225.

12b. *tert*-Butyldiphenylsilyl chloride (535 mg, 1.95 mmol) was added in two equal portions to a stirred solution of hydroquinone (1.0 g, 9.1 mmol), dry DMF (2 mL), CH_2Cl_2 (10 mL), and imidazole (1.5 g, 22 mmol); the second portion was added after 10 min. Conventional extractive workup followed by flash chromatography on silica gel eluted with a solvent gradient beginning with PE and ending with PE/CH_2Cl_2/EtOAc (95:5:2) afforded **12b** (380 mg, 56% based on silyl chloride): IR (neat) 1505 (s), 1425 (s), 1240

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(9) Hine, J. *Structural Effects on Equilibrium in Organic Chemistry*; Wiley: New York, 1975.

(10) The reduced rate of hydrolysis of alkyl silyl ketals may be related to delocalization of the electron pairs of the oxygen on the silyloxy group. Such a delocalization effect has been considered in explaining the poor chelating ability of siloxy oxygens toward Lewis acids.[11,12] Mechanistic studies directed at understanding this effect are in progress and will be reported separately.

(11) Frye, S. V.; Eliel, E. L. *Tetrahedron Lett.* **1986**, *27*, 3223.

(12) (a) Kahn, S. D.; Keck, G. E.; Hehre, W. J. *Tetrahedron Lett.* **1987**, *28*, 279. (b) Keck, G. E.; Castellino, S. *Tetrahedron Lett.* **1987**, *28*, 281.

(13) Melting points were determined in capillaries in a Thomas-Hoover Unimelt apparatus and are uncorrected. Infrared spectra were determined on a Perkin-Elmer Model 283B spectrometer on KBr disks unless otherwise noted. Routine ^1H NMR spectra were determined at 80 MHz on an IBM NR 80 spectrometer with deuteriochloroform as solvent and residual chloroform as standard. Mass spectral and exact mass measurements were obtained by Richard Weisenberger on a Kratos MS-30 spectrometer. The FAB spectra were determined on the above instrument with xenon gas at a potential of 8000 V with a Ion-Tek gun. A 50:50 mixture of glycerol and thioglycerol was used as matrix with methanol and chloroform as solvent. The peak intensities are reported relative to glycerol. Combustion analyses were determined by Scandinavian Microanalytical Laboratories, Helev, Denmark. Alumina and silica gel were obtained from E. Merck Co. Tetrahydrofuran was purified by distillation from benzophenone ketyl. The term "standard workup" refers to drying the solvent over Na_2SO_4, concentration in vacuo, and drying at ca. 0.5 mmHg until the weight is constant. The *tert*-butyldiphenylsilyl chloride[14] and *tert*-butyldimethylsilyl chloride[15] were freshly prepared via published procedures. All other compounds used in this work were either commercially available or else reference is given to their preparation in the Experimental Section. Throughout the Experimental Section, the following abbreviations are used: petroleum ether, bp 35–60 °C (PE), diethyl ether (Et_2O), tetrahydrofuran (THF), dimethyl sulfoxide (Me_2SO), ethyl acetate (EtOAc), and dimethylformamide (DMF).

(14) Hanessian, S.; Lavalle, P. *Can. J. Chem.* **1975**, *53*, 2975.

(15) Corey, E. J.; Venkateswarlu, A. *J. Am. Chem. Soc.* **1972**, *94*, 6190. Ogilive, K. K.; Iwacha, D. J. *Tetrahedron Lett.* **1973**, 317.

(s, br), 1110 (s), 920 (s), 815 (s), 695 cm^{-1} (s); ^{1}H NMR δ 7.7–7.6 (m, 4 H), 7.5–7.3 (m, 6 H), 6.63 (d, J_{AB} = 8.8 Hz, 2 H), 6.55 (d, J_{AB} = 8.8 Hz, 2 H), 4.60 (br s, 1 H), 1.08 (s, 9 H); mass spectrum, exact mass for $C_{22}H_{24}O_2Si$ calcd *m/e* 348.1545, obsd *m/e* 348.1550.

12c. *tert*-Butyldiphenylsilyl chloride (7.47 g, 27 mmol) in THF (25 mL) was added to a −47 °C solution of methylhydroquinone (4 g, 32 mmol) and imidazole (4 g, 59 mmol) in THF (25 mL) over a period of 15 min. After a few milliliters had been added, a thick white paste formed, and it was necessary to swirl the reaction mixture by hand to accomplish mixing. The solution was allowed to warm to room temperature, and after 1.5 h the slurry was poured into water (150 mL) and extracted with PE (3 × 50 mL). Workup gave a tan oil (10.40 g). A sample (6.60 g) of the crude product was purified by careful flash chromatography (20 × 4 cm column, 10% EtOAc/PE as eluant), affording the desired **12c** (2.75 g, 45 %): IR (neat) 1500 (s), 1430 (s), 1190 (s, br), 1110 (s), 850 (s), 700 cm^{-1} (s); ^{1}H NMR δ 7.77–7.65 (m, 4 H), 7.41–7.32 (m, 6 H), 6.6 (br, 1 H), 6.43 (br, 2 H), 4.32 (s, 1 H), 2.07 (s, 3 H), 1.09 (s, 9 H); mass spectrum, exact mass for $C_{23}H_{26}O_2Si$ calcd *m/e* 362.1702, obsd *m/e* 362.1691.

12d. *tert*-Butyldiphenylsilyl chloride (1.50 mL, 1.58 g, 5.8 mmol) in THF (3.5 mL) was added to a −78 °C stirred solution of trimethylhydroquinone (1.0 g, 6.6 mmol), imidazole (1.0 g), and THF (25 mL) over a period of 5 min. After 0.5 h the milky-yellow mixture was allowed to warm to room temperature and was stirred for 12 h. TLC (30% Et_2O/PE as eluant) indicated the presence of some unreacted trimethylhydroquinone, silyl ether, and trimethylquinone. Concentration gave a dark, thick liquid, which was purified by silica gel chromatography (20 × 3.8 cm, 3% Et_2O in PE as eluant). A small amount of trimethylquinone (ca. 100 mg) and silylated trimethylhydroquinone (2.0 g, 90%) was obtained: IR (neat) 2960 (m), 2935 (m), 2860 (m), 1475 (s), 1430 (s), 1330 (m), 1235 (m), 1115 (s), 1090 (m), 882 (s), 703 cm^{-1} (s); ^{1}H NMR δ 7.79–7.67 (m, 4 H), 7.42–7.33 (m, 6 H), 6.09 (br, 1 H), 4.15 (s, 1 H), 2.30 (br, 3 H), 2.18 (br, 3 H), 1.85 (br, 3 H), 1.11 (s, 9 H); mass spectrum, exact mass for $C_{25}H_{30}O_2Si$ calcd *m/e* 390.2015, obsd *m/e* 390.2003.

Anodic Oxidation of Monosilylated Hydroquinones. General. The anodic oxidations were conducted in a single cell by using a Kepco Power Supply MOD JQE 36-3M and a platinum cylindrical anode (3.5 cm diameter × 5 cm high) and cathode (2.5 cm diameter × 5 cm high). The reactions were monitored by TLC or by UV spectroscopy. Reactions monitored by UV spectroscopy were terminated when the UV absorption stopped decreasing. The electrolysis solution was concentrated under vacuum at room temperature, and the residue was treated as described for the individual compounds.

13a. A −10 °C solution of **12a** (180 mg, 0.8 mmol) and 2% $LiClO_4$ in CH_3OH (125 mL) was electrolyzed at 0.05 A. The reaction was terminated after 50 min (97% current efficiency). The residue was partitioned between water (15 mL) and CH_2Cl_2 (3 × 8 mL). Standard workup gave the crude monoketal (150 mg) as a brown oil. Purification of this oil by chromatography on neutral alumina (8 × 2 cm column, 10% Et_2O/PE as eluant) afforded **13a** (117 mg, 58%) as a clear oil: IR (neat) 2960 (s), 2935 (s), 1680 (s), 1640 (s), 1130 (s), 1112 (s), 1062 (s), 1040 (s), 995 (s), 835 (s), 775 cm^{-1} (s); ^{1}H NMR δ 6.67 (J_{AB} = 10.3 Hz, 2 H), 6.13 (J_{AB} = 10.3 Hz, 2 H), 3.29 (s, 3 H), 0.88 (s, 9 H), 0.11 (s, 6 H); mass spectrum, exact mass for $C_{13}H_{22}O_3Si$ calcd *m/e* 254.1338; obsd *m/e* 254.1306.

13b. A −14 °C solution of **12b** (113 mg, 0.325 mmol) in 2% $LiClO_4$ in CH_3OH (100 mL) was electrolyzed at 0.05 A for 25 min (84% current efficiency). The residue was poured into water (50 mL) and extracted with CH_2Cl_2 (4 × 25 mL). Standard workup afforded crude **13b** (99 mg) as a yellow oil, which was purified by chromatography on neutral alumina (8 × 2 cm column). Gradient elution first with PE and then with 10% Et_2O/PE gave **13b** (74 mg, 60%): IR (neat) 2930 (s), 1679 (s), 1638 (s), 1428 (s), 1110 (s), 1065 (s), 1035 (s), 990 (s), 840 (s), 700 cm^{-1} (s); ^{1}H NMR δ 7.74–7.62 (m, 4 H), 7.40–7.24 (m, 6 H), 6.58 (d, J_{AB} = 10.4 Hz, 2 H), 5.86 (d, J_{AB} = 10.4 Hz, 2 H), 3.32 (s, 3 H), 1.05 (s, 9 H); mass spectrum, exact mass for $C_{19}H_{18}O_3Si$ ($M^+ - C_4H_8$) calcd *m/e* 322.1025, obsd *m/e* 322.1028.

13c. The silyl ether **12c** (0.629 g, 1.74 mmol) and lutidine (0.5 mL) were dissolved in Et_2O (4 mL), and 2% $LiClO_4$ in CH_3OH (100 mL) was added. The electrolysis was conducted at −7 °C at 0.1 A for 2 h (current efficiency 47%). The residue was partitioned between brine (20 mL), water (20 mL), Et_2O (20 mL), and PE (20 mL). The organic portion was washed with 5% acetic acid (30 mL), 5% $NaHCO_3$ (2 × 30 mL), and brine (20 mL) and then dried over Na_2SO_4. Evaporation of the solvents left a dark oil (0.671 g), smelling of lutidine, which was chromatographed on silica gel [11 × 2 cm, eluted with 2% EtOAc (200 mL), 3% EtOAc (100 mL), and 5% ethyl acetate in PE (100 mL)], affording **13c** (361 mg, 53%). **13c**: IR (neat) 2965 (m), 2935 (m), 1688 (s), 1658 (s), 1433 (m), 1118 (s), 1086 (s), 1070 (m, sh), 1035 (s), 1010 (m), 1000 (m, sh), 966 (m), 701 cm^{-1} (s); ^{1}H NMR δ 7.76–7.53 (m, 4 H), 7.41–7.28 (m, 6 H), 6.65 (dd, J = 3, 10 Hz, 1 H), 6.57 (hextet, J = 3 Hz, 1 H), 5.88 (d, J_{AB} = 10 Hz, 1 H), 3.35 (s, 3 H), 1.52 (d, J = 1.4 Hz, 3 H), 1.04 (s, 9 H). Anal. Calcd for $C_{24}H_{28}O_3Si$: C, 73.41; H, 7.19. Found: C, 73.20; H, 7.17.

13d. A −10 °C solution of **12d** (0.610g, 1.6 mmol), 2% $LiClO_4$ in CH_3OH (100 mL), and lutidine (2 drops) was electrolyzed at 0.1 A for 1.5 h (57% current efficiency). The residue was partitioned between water (30 mL), PE (20 mL), and Et_2O (20 mL). The organic portion was washed once with 5% $NaHCO_3$ (30 mL) and brine (20 mL) and dried over Na_2SO_4. Concentration in vacuo afforded the crude monoketal (613 mg), which was purified by filtration through silica gel (10 × 2 cm column, Et_2O/PE 10% as eluant), affording pure monoketal **13d** (0.503 g, 77%) as a pale yellow oil: IR (neat) 2960 (m), 2940 (m), 1655 (s), 1430 (m), 1111 (s), 1085 (s), 1060 (s), 1000 (m), 960 (m), 700 cm^{-1} (s); ^{1}H NMR δ 7.81–7.30 (m, 10 H), 6.61 (d, J = 1.5 Hz, 1 H), 3.04 (s, 3 H), 1.95 (d, J = 1 Hz, 3 H), 1.67 (d, J = 1 Hz, 3 H), 1.44 (d, J = 1.5 Hz, 3 H), 1.02 (s, 9 H). Anal. Calcd for $C_{26}H_{32}O_3Si$: C, 74.23; H, 7.67. Found: C, 74.02; H, 7.70.

Preparation of Silylated Hydroquinone Ethers. 14a. A 25 °C solution of *p*-methoxyphenol (1.62 g, 13.1 mmol) and imidazole (1.8 g, 26 mmol) in THF (25 mL) was added to *tert*-butyldimethylsilyl chloride (2.01 g, 13.3 mmol). After the mixture was stirred for 15 min, the thick white mixture was diluted with water (50 mL) and extracted with Et_2O (3 × 15 mL). Concentration afforded nearly pure silyl ether (2.96 g, 95%) as a yellow oil. A small sample was chromatographed on silica gel (8 × 2 cm column, 5% Et_2O/PE as eluant), affording a clear oil: IR (neat) 2950 (m), 2930 (m), 1510 (s), 1255 (m), 1235 (s), 920 (m), 910 (m), 839 (m), 829 cm^{-1} (m); ^{1}H NMR δ 6.74 (s, 4 H), 3.74 (s, 3 H), 0.96 (s, 9 H), 0.15 (s, 6 H); mass spectrum, exact mass for $C_{13}H_{22}O_2Si$ calcd *m/e* 238.1389, obsd *m/e* 238.1404.

14b. *tert*-Butyldiphenylsilyl chloride (2.45 g, 8.9 mmol) was added to a solution of *p*-methoxyphenol (1.0 g, 8.06 mmol) and imidazole (1 g, 15 mmol) in dry acetonitrile (5 mL). The reaction mixture warmed noticeably, and a white solid precipitated. After the mixture was stirred for 10 min, the slurry was poured into Et_2O (30 mL) and washed with water (4 × 20 mL). Standard workup gave **14b** (2.91 g, 100%) as a white solid, mp 59–63 °C. A sample (500 mg) was recrystallized from EtOH (3 mL) to give white crystals (390 mg): mp 69.5–71 °C; IR (KBr) 2955 (m), 2930 (m), 2855 (m), 1505 (s), 1445 (m), 1430 (s), 1240 (br, s), 1110 (s), 1100 (s), 1035 (s), 920 (s), 830 (s), 800 (s), 700 (s), 500 cm^{-1} (s); ^{1}H NMR δ 7.76–7.64 (m, 4 H) 7.41–7.33 (m, 6 H), 6.64 (s, 4 H), 3.67 (s, 3 H), 1.08 (s, 9 H); mass spectrum, exact mass for $C_{23}H_{26}O_2Si$ calcd *m/e* 362.1703, obsd *m/e* 362.1703.

14c. Dimethyl sulfate (1.9 g, 15 mmol) was added to a mixture of **12c** (2.75 g, 7.59 mmol), K_2CO_3 (3 g), and acetone (30 mL). The solution was refluxed for 4 h, cooled, poured into water (160 mL), and extracted with CH_2Cl_2 (3 × 30 mL). Standard workup afforded crude **14c** contaminated with dimethyl sulfate (2.85 g). The oil was dissolved in 5% Et_2O/PE (3 mL) and filtered through silica gel (15 × 3 cm column, 5% Et_2O/PE as eluant), to afford **14c** (2.57 g, 90%): IR (neat) 2950(m), 2930 (m), 2850 (m), 1500 (s), 1465 (m), 1430 (m), 1285 (m), 1225 (s), 1180 (m), 1110 (s), 1038 (m), 1009 (m), 970 (m), 840 (s), 700 cm^{-1} (s); ^{1}H NMR δ 7.79–7.67 (m, 4 H), 7.41–7.33 (m, 6 H), 6.65 (br, 1 H), 6.49 (br, 2 H), 3.70 (s, 3 H), 2.08 (s, 3 H), 1.10 (s, 9 H); mass spectrum, exact mass for $C_{24}H_{28}O_2Si$ calcd *m/e* 376.1859, obsd *m/e* 376.1855.

14d. *tert*-Butyldiphenylsilyl chloride (3.6 g, 3.4 mL, 13.1 mmol) in THF (6 mL) was slowly added to a −78 °C solution of trimethylhydroquinone (2.0 g, 13.1 mmol), imidazole (2.0 g, 29 mmol), and THF (40 mL). After the addition was complete (ca. 4 min), the reaction mixture was stirred for 5 min at −78 °C, then allowed to warm to room temperature, and stirred for 4 h. The brown slurry was poured into brine (60 mL) and extracted with Et_2O (30 mL). The Et_2O layer was washed once with brine (30 mL), dried over Na_2SO_4, and evaporated, leaving a heavy brown oil (5.1 g), which was dissolved in acetone (50 mL). Potassium carbonate (5.5 g, 40 mmol, powdered) and dimethyl sulfate (3.3 g, 2.5 mL, 26 mmol) were added. The vigorously stirred solution was maintained at reflux under N_2 for 12 h. After the majority of the acetone had been removed under reduced pressure, the brown slurry was partitioned between PE (50 mL) and water (40 mL). The organic layer was washed with water (3 × 20 mL) and brine (20 mL), dried over Na_2SO_4, and concentrated in vacuo to give crude **14d** (5.4 g). Silica gel chromatography (18 × 3 cm column, PE as eluant) afforded **14d** (4.20 g, 80%): IR (neat) 2935 (m), 2860 (m), 1480 (s), 1460 (m), 1400 (m), 1325 (m), 1230 (s), 1115 (s), 1090 (s), 1010 (m), 870 (s), 700 cm^{-1} (s); ^1H NMR δ 7.79–7.67 (m, 4 H), 7.46–7.34 (m, 6 H), 6.11 (br, 1 H), 3.59 (s, 3 H), 2.28 (br, 3 H), 2.21 (br, 3 H), 1.89 (br, 3 H), 1.11 (s, 9 H); mass spectrum, exact mass for $C_{26}H_{32}O_2Si$ calcd m/e 404.2172; obsd m/e 404.2174.

14e. A solution of 2-hydroxy-5-methoxybenzaldehyde (1.5 g, 10 mmol), dry CH_3OH (15 mL), trimethyl orthoformate (5 mL, 5.15 g, 49 mmol), and *p*-toluenesulfonic acid (20 mg) was stirred for 10 min. The reaction was complete after 2 min as evidenced by the disappearance of the yellow color of the benzaldehyde. The reaction mixture was neutralized with powdered K_2CO_3, poured into 1:1 brine/5% $NaHCO_3$ (40 mL), and extracted with PE (2 × 40 mL). Standard workup gave a clear oil, to which was added imidazole (1.5 g, 23 mmol) and THF (15 mL). *tert*-Butyldiphenylsilyl chloride (3.5 mL, 13 mmol) was added to this stirred solution. After being stirred overnight, the white slurry was poured into 5% NaOH (50 mL) and extracted with PE (2 × 30 mL). The combined organic portions were washed once with brine (20 mL) and evaporated under reduced pressure, affording a clear, thick oil (4.25 g, 100%) that solidified after addition of CH_3OH (10 mL) and cooling, mp 60–75 °C. The crude product was recrystallized from a minimum amount of hot CH_3OH, affording white, crystalline acetal (3.9 g, 90%): mp 93–95 °C; IR (KBr) 1500 (s), 1280 (s), 1225 (s), 1165 (s), 1115 (s), 1085 (s), 1053 (s), 1040 (s), 920 (s), 908 (s), 695 cm^{-1} (s); ^1H NMR δ 7.74–7.66 (m, 4 H), 7.40–7.24 (m, 6 H), 7.08 (br, 1 H), 6.37 (br, 2 H), 5.83 (br, 1 H), 3.69 (s, 3 H), 3.39 (s, 6 H), 1.09 (s, 9 H); mass spectrum, exact mass for $C_{26}H_{32}O_4Si$ calcd m/e 436.2070, obsd m/e 436.2061.

14f. *tert*-Butyldiphenylsilyl chloride (3.0 mL, 3.2 g, 11.6 mmol) was added to a solution of 3-bromo-4-methoxyphenol[2] (1.8 g, 8.9 mmol), imidazole (1.14 g, 16.8 mmol), and THF (20 mL); a white precipitate began to form immediately. After being stirred for 5 h, the slurry was diluted with PE (50 mL) and washed with 1:1 brine/water (2 × 20 mL), 10% KOH (2 × 20 mL), and brine (25 mL). Standard workup gave a dark oil (4.7 g) showing four spots on TLC. The polar, colored impurities were removed by filtration through silica gel (15 × 3 cm column, 5% EtOAc/PE as eluant), affording a clear oil (3.13 g, 80%). A small sample of the oil was crystallized from PE/$CHCl_3$: mp 51–54 °C; IR (KBr) 1490 (s), 1275 (s), 1215 (s), 1111 (m), 945 (s), 810 (m), 695 (s), 495 cm^{-1} (m); ^1H NMR δ 7.76–7.64 (m, 4 H), 7.46–7.34 (m, 6 H), 7.09–7.05 (distorted t, 1 H), 6.57 (s, 1 H), 6.55 (s, 1 H), 3.74 (s, 3 H), 1.09 (s, 9 H); mass spectrum, exact mass for $C_{23}H_{25}BrO_2Si$ calcd m/e 442.0787, obsd m/e 442.0796.

14g. *tert*-Butyldiphenylsilyl chloride (1.5 g, 5.5 mmol) was added to a solution of 3,4-dimethoxyphenol (0.832 g, 5.4 mmol), imidazole (0.9 g), and THF (50 mL) at 25 °C. This solution was stirred for 3 h, then poured into 1:1 brine/water (40 mL), and extracted with PE. The PE was washed with 1:1 brine/water (2 × 20 mL) and then brine (20 mL), dried over Na_2SO_4, and evaporated, affording crude silyl ether (2.1 g). Chromatography on silica gel (12 × 3 cm column, 20% CH_2Cl_2/PE as eluant) afforded a clear semisolid (1.80 g, 85%): IR (neat) 2960 (s), 2930 (s), 1510 (s), 1465 (s), 1450 (s), 1430 (s), 1228 (s), 1200 (s), 1160 (s), 1110 (s), 1038 (s), 980 (s), 848 (s), 838 (s), 695 cm^{-1} (s); ^1H NMR δ 7.78–7.61 (m, 4 H), 7.47–7.28 (m, 6 H), 6.58 (d, J_{AB} = 8.5 Hz, 1 H), 6.33 (s, 1 H), 6.26 (d, J_{AB} = 8.5 Hz, 1 H), 3.75 (s, 3 H), 3.57 (s, 3 H), 1.12 (s, 9 H); mass spectrum, exact mass for $C_{24}H_{28}O_3Si$ calcd m/e 392.1807, obsd m/e 392.1825.

16. *tert*-Butyldiphenylsilyl chloride (4.0 g, 14.5 mmol) was added to a 0 °C solution of 2-methoxyphenol (2.0 g, 16.1 mmol), imidazole (2.2 g, 32.2 mmol), and THF (20 mL). This solution was stirred at 0 °C for 30 min, then stirred at 40 °C for 10 min, cooled, diluted with brine (50 mL), and extracted with CH_2Cl_2 (3 × 20 mL). Standard workup gave crude silyl ether (5.8 g), which was purified by filtration through silica gel (15 × 3 cm column, 5% Et_2O/PE as eluant) to give pure silyl ether (3.9 g, 74%) as a colorless oil: IR (neat) 1505 (s), 1283 (s), 1265 (s), 1228 (s), 1115 (s), 740 (s), 696 cm^{-1} (s); ^1H NMR δ 7.81–7.69 (m, 4 H), 7.44–7.24 (m, 6 H), 6.89–6.63 (structured m, 4 H), 3.57 (s, 3 H), 1.15 (s, 9 H); mass spectrum, exact mass for $C_{19}H_{17}O_2Si$ ($M^+ - C_4H_9$) calcd m/e 305.0998, obsd m/e 305.0976.

18. *tert*-Butyldiphenylsilyl chloride (2.5 mL, 2.6 g, 9.5 mmol) was added to a solution of 4-methoxy-1-naphthol (1.0 g, 5.7 mmol), imidazole (0.8 g, 12 mmol), and THF (25 mL), and the solution was stirred for 2 h. At the end of this period, the white slurry was poured into 1:1 water/brine (40 mL) and extracted with PE (3 × 20 mL). Workup gave a semisolid, which was triturated with CH_3OH to afford **18** (1.70 g, 72%) sufficiently pure for subsequent chemistry. A small sample was recrystallized from CH_3OH, affording white crystals: mp 99–100 °C; IR (KBr) 1597 (m), 1468 (s), 1430 (m), 1390 (s), 1275 (s), 1241 (m), 1115 (m), 1100 (s), 1070 (s), 855 (s), 803 (m), 765 (m), 705 (s), 695 (s), 510 cm^{-1} (m); ^1H NMR δ 8.60–8.15 (m, 2 H), 7.90–7.25 (m, 12 H), 6.35 (s, 2 H), 3.85 (s, 3 H), 1.20 (s, 9 H); mass spectrum, exact mass for $C_{27}H_{28}O_2Si$ calcd m/e 412.1859, obsd m/e 412.1838.

Anodic Oxidation of Silylated Hydroquinone Ethers. General. The electrodes and power supply were those noted earlier. Reactions were monitored by UV spectroscopy or TLC. In the cases in which UV spectroscopy was used, the reaction was terminated when the absorption at ca. 290 nm stopped decreasing. Several chips of dry ice were added to the reaction mixture to neutralize the potassium hydroxide, the methanol was removed in vacuo below 30 °C, and the residue was treated as described below.

15a. A solution of **14a** (79 mg, 0.33 mmol) in 1% methanolic KOH (100 mL) was electrolyzed at −16 °C at a constant current of 0.15 A for 18 min (39% current efficiency). The residue was diluted with water (15 mL) and extracted with CH_2Cl_2 (3 × 15 mL). Standard workup afforded the crude bisketal **15a** (0.0817 g, 82%) as a yellow oil. This oil was further purified by chromatography on neutral alumina (8 × 2 cm column, 10% Et_2O/PE as eluant), affording the pure bisketal (52 mg, 52%) as a nearly colorless oil: IR (neat) 2955 (m), 2935 (m), 1130 (m), 1110 (s), 1065 (m), 1040 cm^{-1} (m); ^1H NMR δ 5.95 (s, 4 H), 3.26 (s, 6 H), 3.21 (s, 3 H), 0.85 (s, 9 H), 0.08 (s, 6 H); mass spectrum, exact mass for $C_{15}H_{28}O_4Si$ calcd m/e 300.1757, obsd m/e 300.1757.

15b. A −15 °C solution of **14b** (343 mg, 0.95 mmol) in 1% methanolic KOH was oxidized at 0.05 A for 103 min (59% current efficiency). The residue was poured into water (40 mL) and extracted with CH_2Cl_2 (4 × 15 mL). Standard workup gave **15b** (387 mg, 96%) as a clear oil: IR (neat) 2940 (s), 2860 (s), 1430 (s), 1405 (s), 1110 (s, br), 1065 (s, br), 1035 (s, br), 975 (s, br), 960 (s), 700 cm^{-1} (s); ^1H NMR δ 7.78–7.64 (m, 4 H), 7.42–7.30 (m, 6 H), 5.91 (d, J_{AB} = 10.6 Hz, 2 H), 5.80 (d, J_{AB} = 10.65 Hz, 2 H), 3.21 (s, 3 H), 3.19 (s, 3 H), 3.12 (s, 3 H), 1.02 (s, 9 H); FAB mass spectrum, m/e 424 (M^+).

15c. A −14 °C solution of **14c** (490 mg, 1.3 mmol) in 1% methanolic KOH (100 mL) was electrolyzed at 0.03 A for about 2 h. The pale greenish CH_3OH solution was concentrated, and the residue was poured into water (50 mL) and extracted with CH_2Cl_2 (4 × 10 mL). Workup afforded crude **15c** (0.532 g, 92%) as a dark yellow oil. Although the ^1H NMR spectrum of the crude product showed negligible impurities, a sample was prepared for analysis by chromatography on base-washed silica gel (2 × 5 cm column, 10% Et_2O/PE as eluant): IR (neat) 2930 (s), 2890 (m), 2850 (m), 1425 (m), 1390 (m), 1200 (m), 1145 (m), 1105 (s, br), 1080 (s, br), 1032 (m), 1020 (m), 995 (m), 960 (s), 815 (m), 735 (m), 695 cm^{-1} (s); ^1H NMR δ 7.74–7.65 (m, 4 H), 7.40–7.30 (m, 6 H), 6.15 (d, J_{AB} = 2.6 Hz, 0.5 H), 6.03 (d, J_{AB} = 2.6 Hz, 0.5 H), 5.77 (str m, 1 H), 5.65 (d, J_{AB} = 10.1 Hz, 1 H), 3.19 (s, 3 H), 3.07 (s, 3 H), 2.89 (s, 3 H), 1.55 (d, J = 1.4 Hz, 3 H), 1.02 (s, 9 H). Anal. Calcd for $C_{26}H_{34}O_4Si$: C, 71.18; H, 7.82. Found: C, 71.45; H, 7.83.

15d. A −10 °C solution of **14d** (0.710 g, 1.76 mmol) in Et_2O (3 mL) and 1% methanolic KOH (80 mL) was electrolyzed at a constant current of 0.08 A for 2 h (59% current efficiency). The residue was partitioned between Et_2O (40 mL) and 1:1 water/brine (40 mL). The aqueous portion was washed once with PE (30 mL), and the combined organic portions were dried over Na_2SO_4 and evaporated, affording a clear, yellow oil (1.18 g). The crude bisketal was purified by chromatography on base-washed silica gel (10 × 2 cm, 9:1 PE/Et_2O as eluant), affording pure bisketal (639 mg, 78%) as a clear oil. The material crystallized in the refrigerator over several weeks: mp 69–74 °C; IR (neat) 2940 (s), 1140 (s), 1108 (br, sh), 1080 (s), 740 (s), 702 cm^{-1} (s); ^1H NMR δ 7.8–7.6 (m, 4 H), 7.5–7.3 (m, 6 H), 5.37 (q, J = ca. 1 Hz, 1 H), 2.89 (s, 6 H), 2.82 (s, 3 H), 1.86 (d, J = ca. 1 Hz, 3 H), 1.65 (d, J = ca. 1 Hz, 3 H), 1.41 (d, J = 1.5 Hz, 3 H), 1.04 (s, 9 H). Anal. Calcd for $C_{28}H_{32}O_4Si$: C, 72.04; H, 8.21. Found: C, 72.10; H, 8.22.

15e. A -5 °C slurry of **14e** (1.007 g, 2.310 mmol) in 1% methanolic KOH (100 mL) was electrolyzed at 0.1 A for 3.5 h (35 % current efficiency). At the end of the electrolysis nearly all of the solid had dissolved, and the crude pale yellow semisolid was partitioned between water (40 mL) and 1:1 Et_2O/PE (40 mL). Standard workup gave a pale yellow, slightly gummy solid (1.102 g, 96% crude). Three recrystallizations from CH_3OH (4 mL) afforded a white solid of high purity (0.808 g, 70%): mp 94–95 °C; IR (KBr) 1395 (m), 1150 (m), 1110 (s), 1065 (s), 705 cm^{-1} (m); ^1H NMR δ 7.87–7.59 (m, 4 H), 7.42–7.29 (m, 6 H) 6.35 (br d, J = 2.7 Hz, 1 H), 5.75 (dd, J = 10.5 Hz, 2.7 Hz, 2 H), 5.43 (J_{AB} = 10.5 Hz, 1 H), 5.17 (br s, 1 H), 3.38 (s, 3 H), 3.33 (s, 3 H), 3.25 (s, 3 H) 3.20 (s, 3 H), 2.92 (s, 3 H), 1.03 (s, 9 H). Anal. Calcd for $C_{28}H_{38}O_6Si$: C, 67.42; H, 7.69. Found: C, 67.45; H, 7.76.

17. A -14 °C solution of **16** (1.00 g, 2.76 mmol) in 1% methanolic KOH (80 mL) was electrolyzed at 0.1 A for 5 h (30% current efficiency). The residue was taken up with water (50 mL) and extracted with CH_2Cl_2 (3 × 30 mL). The combined organic phases were washed once with 5% $NaHCO_3$ (40 mL). Standard workup gave a dark oil (1.03 g), which was chromatographed on neutral, activity III alumina (10 × 2 cm column, PE as eluant), affording pure 17 (220 mg, 19%): IR (neat) 2940 (m), 2860 (m), 1430 (m), 1150 (s, br), 1085 (s, br), 1055 (s, br), 1000 (m), 700 cm^{-1} (s); ^1H NMR δ 7.87–7.72 (m, 4 H), 7.40–7.28 (m, 6 H), 5.83–5.78 (m, 2 H), 5.60–5.51 (m, 2 H), 3.46 (s, 3 H), 3.41 (s, 3 H), 3.18 (s, 3 H), 1.07 (s, 9 H). Anal. Calcd for $C_{25}H_{32}O_4Si$: C, 70.70; H, 7.60. Found: C, 70.90; H, 7.69.

19. A solution of 18 (0.472 g, 1.145 mmol) in THF (10 mL) was added to 1% methanolic KOH (60 mL), and the solution was cooled to -5 °C and oxidized at a current of 0.1 A. After 45 min (82% current efficiency), TLC showed the absence of starting material. The residue was poured into water (40 mL) and extracted with 1:1 Et_2O/PE (30 mL). Standard workup gave a dark oil (0.550 g). The crude bisketal was purified by column chromatography on base-washed silica gel (2 × 9 cm, 10% Et_2O/PE as eluant), affording pure bisketal (383 mg, 71%) as a clear, thick oil. Continued elution afforded bisketal (74 mg) contaminated with other products. Upon standing, the pure bisketal solidified and was recrystallized from Et_2O/PE, affording very large, clear hexagonal plates: mp 95–97 °C; IR (KBr) 2975 (m), 2935 (m), 1387 (m), 1298 (m), 1288 (m), 1147 (s), 1115 (s), 1080 (s), 1035 (s), 1000 (m), 780 (m), 945 (s), 710 (s), 610 cm^{-1} (m); ^1H NMR δ 7.89–7.29 (m, 16 H), 5.95 (J_{AB} = 10.6 Hz, 1 H), 5.84 (J_{AB} = 10.6 Hz, 1 H), 3.11 (s, 3 H), 2.97 (s, 3 H), 2.92 (s, 3 H), 1.04 (s, 9 H). Anal. Calcd for $C_{29}H_{34}O_4Si$: C, 73.36; H, 7.22. Found: C, 73.21; H, 7.30.

Desilylation of 15a. To a -78 °C solution of **15a** (100 mg, 0.33 mmol) in dry THF (1 mL) was added dropwise (n-Bu)$_4$NF (1.0 mL, 1.0 mmol). After 5 min, the reaction mixture was allowed to come to room temperature, and toluene (6 mL) was added. The THF was removed in vacuo, and the remaining toluene solution was chromatographed on silica gel (2 × 6 cm column, 3:7 Et_2O/PE eluant) to give 4,4-dimethoxy-2,5-cyclohexadienone (39 mg, 76%) as a clear oil, which showed spectroscopic properties identical with those of an authentic sample.

Desilylation of 15b. To a 0 °C solution of **15b** (110 mg, 0.259 mmol) in THF (5 mL) was added (n-Bu)$_4$NF (1.0 mL, 1.0 mmol). After ca. 1.5 min the solution turned dark, and the reaction was quenched with water (1.5 mL). The reaction mixture was poured into water (50 mL) and extracted with CH_2Cl_2 (4 × 8 mL). Standard workup and chromatography as described above gave 4,4-dimethoxy-2,5-cyclohexadienone (32 mg, 80%) identified as above.

Monohydrolysis of Quinone Bisketals 15a–c and 19a. The following general procedure was used for the monohydrolyses. To a room temperature ca. 0.03 M solution of the compound in acetone was added ca. one-third the volume of 6% aqueous acetic acid, and the reaction mixture was stirred for the indicated time. The reaction was quenched by pouring into a 5% $NaHCO_3$ solution, the organic product was extracted with methylene chloride, and the organic solution was dried over Na_2SO_4. Concentration in vacuo gave the monoketal showing identical spectroscopic properties with an analytical sample. The following are the reaction times and yields for the quinone bisketals above.

13a. Reaction of **15a** as described above for 4 h gave **13a** (97%), which showed spectroscopic properties identical with those of **13a** obtained from electrolysis of **12a**.

13b. Reaction of **15b** as described above for 3 h gave **13b** (91%) showing spectroscopic properties identical with those of **13b** obtained from oxidation of **12b**.

13c. Reaction of **15c** as described above for 22 h gave **13c** (89%) showing spectroscopic properties identical with those of **13c** obtained from **12c**.

Methyl *tert*-Butyldiphenylsilyl Ketal of 1,4-Naphthoquinone. Reaction of **19** as described above for 12 h gave the title compound (91%) as a clear oil: IR (neat) 2960 (m), 2940 (m), 1680 (s), 1430 (m), 1300 (s), 1141 (m), 1115 (s), 1060 (s), 1020 (m), 765 (m), 700 cm^{-1} (s); ^1H NMR δ 7.89–7.22 (m, 14 H), 6.62 (d, J_{AB} = 10 Hz, 1 H), 6.02 (d, J_{AB} = 10 Hz, 1 H), 3.11 (s, 3 H), 1.01 (s, 9 H). Anal. Calcd for $C_{27}H_{28}O_3Si$: C, 75.65; H, 6.59. Found: C, 75.57; H, 6.54.

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