η^5-cyclopentadienyl ^{1}H NMR resonances.

Acknowledgment. Financial support from the Air Force Office of Scientific Research through grant no. 91-0197 and Dow Corning Corp. is gratefully acknowledged.

Reductive Aromatization of Quinols. New Convenient Methods for the Regiospecific Synthesis of *p*-Hydroxy *C*-Aryl Glycals

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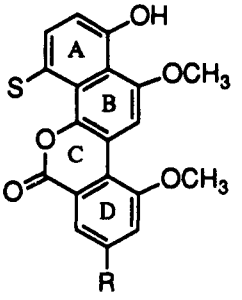
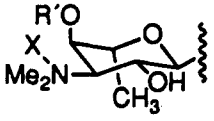
Received May 12, 1992

Among the naturally occurring *C*-aryl glycosides, the gilvocarcin antitumor antibiotics **1**[2] are unique in that the carbohydrate substituent is positioned para to a phenolic hydroxyl group. Implicit in previous approaches to the establishment of this connection is the feasibility of liberating the phenolic hydroxyl group from a *p*-alkoxy *C*-aryl glycoside.[3-7] For simple alkyl phenyl ethers, this dealkylation has not been demonstrated, and successful prepartions of *p*-hydroxy *C*-aryl glycosides have required the use of protecting groups which are more easily removed.[3,6]



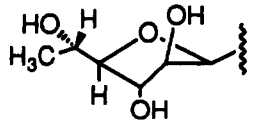
1, The Gilvocarcin *C*-Aryl Glycosides

Ravidomycins R=CH=CH$_2$ S=



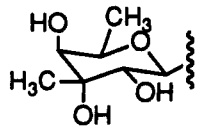
a Ravidomycin R′=Ac, X=electron pair
b Deacetylravidomycin R′=H, X=electron pair
c Deacetylravidomycin N-oxide R′=H, X=O

Gilvocarcins S=



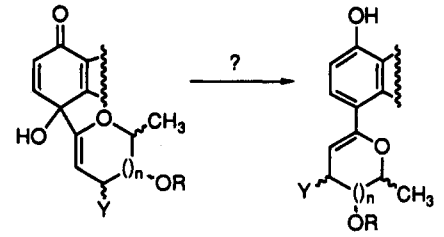
d M R=CH$_3$
e V R=CH=CH$_2$
f E R=CH$_2$CH$_3$

Chrysomycins S=



g A R=CH=CH$_2$
h B R=CH$_3$

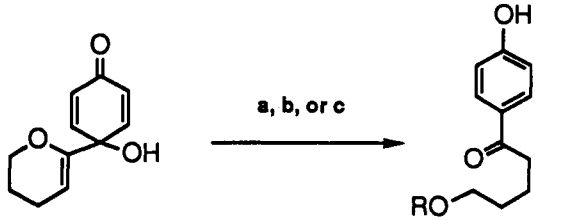
Scheme I



We have been exploring a "reverse polarity" approach in which the reductive aromatization of a quinol glycal would serve as a key step (Scheme I). In this approach, the free phenolic hydroxyl group would be generated directly by the method of synthesis.

In this paper, we are pleased to report the reductive aromatization of benzo- and naphthoquinol glycals. When coupled with the preparation of quinol glycals from quinones and lithio glycal reagents, this transformation provides a regiospecific synthesis of *p*-hydroxyaryl glycals in two simple steps.

Initial efforts to effect this type of transformation had been abandoned following the observation of hydrolytic ring opening in a model system (**2a** → **3** or **4**).[4]



2a

3 R = Ac
4 R = H

a) Zn/HOAc/H_2O b) Al(Hg)/THF/H_2O
c) 1. $NaBH_4$/EtOH, 2. NaOH/Δ

However, more recent experiments have revealed that the desired conversions (Scheme I) may be easily achieved. We have now shown that, under controlled conditions, dithionite solution reduces *p*-benzoquinol glycals to *p*-

(1) Recipient of the 1991–92 Division of Organic Chemistry (American Chemical Society) Graduate Fellowship sponsored by The Rohm and Haas Co.

(2) (a) Gilvocarcins: Takahashi, K.; Yoshida, M.; Tomita, F.; Shirahata, K. *J. Antibiot.* **1981**, *34*, 271. (b) Ravidomycins: Findlay, J.; Liu, J.-S.; Radics, L.; Rakhit, S. *Can. J. Chem.* **1981**, *59*, 3018. Rakhit, S.; Eng, C.; Baker, H.; Singh, K. *J. Antibiot.* **1983**, *36*, 1490. Narita, T.; Matsumoto, M.; Mogi, K.; Kukita, K.-I.; Kawahara, R.; Nakashima, T. *J. Antibiot.* **1989**, *42*, 347. (c) Chrysomycins: Weiss, U.; Yoshihira, K.; Highet, R.; White, R.; Wei, T. *J. Antibiot.* **1982**, *35*, 1194.

(3) Suzuki recently reported the first total synthesis of Gilvocarcin M and revised the absolute configuration of the natural product: Matsumoto, T.; Hosoya, T.; Suzuki, K. *J. Am. Chem. Soc.* **1992**, *114*, 3568.

(4) Numerous *p*-alkoxy *C*-aryl glycosides have been prepared by coupling aryl ethers with carbohydrate derivatives and recently a novel preparation of a *p*-methoxy *C*-phenyl glycoside was reported by us. See: Parker, K. A.; Coburn, C. A. *J. Am. Chem. Soc.* **1991**, *113*, 8516 and references cited therein.

(5) Hart has prepared *p*-methoxy *C*-phenyl glycosides by electrophile-initiated cyclizations of substituted styrenes (D. J. Hart, personal communication).

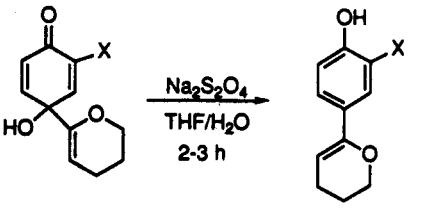
(6) Only recently have *p*-hydroxy *C*-aryl glycosides been prepared. The methods which proved successful required temporary protection of the hydroxyl group. See: Farr, R. N.; Kwok, D.-I.; Daves, G. D., Jr. *J. Org. Chem.* **1992**, *57*, 2093.

(7) For other recent work on *C*-aryl glycoside construction, see: Martin, O. R.; Rao, P.; Kurz, K. G.; El-Shenawy, H. A. *J. Am. Chem. Soc.* **1988**, *110*, 8698 and references cited therein.

0022-3263/92/1957-5547$03.00/0

hydroxy C-phenyl glycals. Both benzo- and naphthoquinol glycals may be converted to the corresponding p-hydroxy C-aryl glycals by aluminum amalgam.

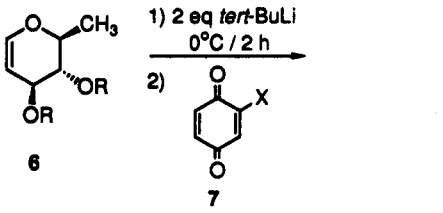
Exposure of quinol **2a** to sodium dithionite in aqueous THF for 2–3 h resulted in clean conversion to p-hydroxyphenyl glycal **5a**. Furthermore, bromoquinol **2b** was converted to phenol **5b** under these conditions.



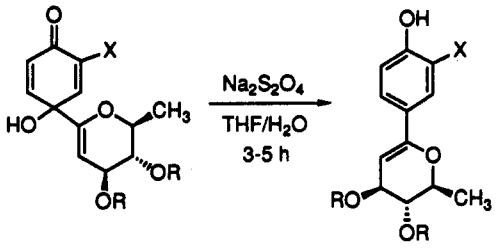
2 **5**

a X = H, 83%
b X = Br, 90%

Of more relevance for our planned application, quinols **8a** and **8b** (derived from protected glycal **6** and the corresponding benzoquinones **7a** and **7b**) afforded phenyl glycals **9a** and **9b**, respectively, when treated with the dithionite solution.



6 **7**

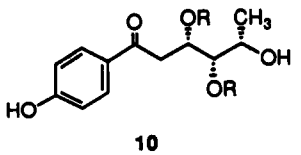


8a 91%
b 78%

9a 84%
b 87%

a X = H, R = TBDMS
b X = Br, R = TBDMS

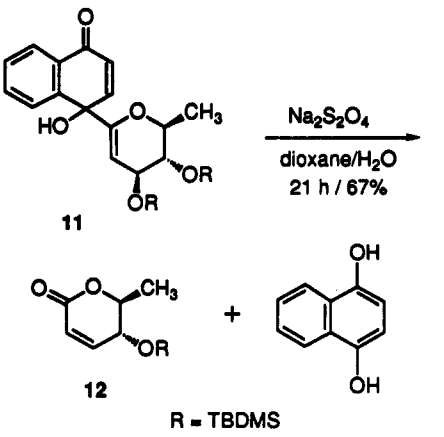
A limitation on the reaction time was found to be essential for the successful isolation of glycal. For example, extended treatment (28 h) of quinol **8b** with the dithionite solution resulted in the isolation of ketone **10** in 90% yield.



10

Attempts to apply the dithionite reduction conditions to naphthoquinol glycals were unsuccessful. Exposure of naphthoquinol **11** to dithionite solution for several hours at room temperature did not lead to the formation of a new product. Furthermore, treatment with dithionite solution for longer times (21 h) resulted in hydrolytic decomposition and the isolation of the α,β-unsaturated lactone **12** (in 67% yield) and 1,4-naphthohydroquinone.

The relative ease of reduction of benzoquinols over that of naphthoquinols is consistent with expectations based on the reduction potentials of the corresponding quinones.[8]



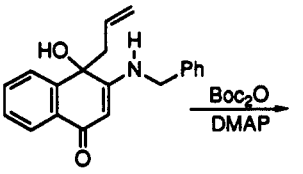
11

12

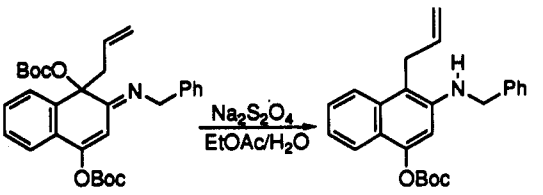
R = TBDMS

Extension of the analogy implies that quinols which are substituted with electron-donating groups will be more difficult to reduce than those which are unsubstituted or which are substituted with electron-withdrawing groups.

In this context, it is interesting to note that quinol **13**, which was inert to hydride reducing agents (including lithium aluminum hydride with or without aluminum chloride, sodium borohydride, diisobutylaluminum hydride, and triethylsilane/trifluoroacetic acid) and resistant to zinc in acetic acid, was successfully converted to the desired naphthol by a two-step procedure in which the cross-conjugated system of quinol **13** was replaced by the linearly conjugated system of the protected enol imine **14**. Thus, treatment of quinol **13** with 2.5 equiv of di-*tert*-butylcarbonate and a catalytic amount of DMAP gave imine **14**. Then sodium dithionite in water/ethyl acetate effected reductive aromatization, affording naphthalene **15** in 70–75% overall yield.

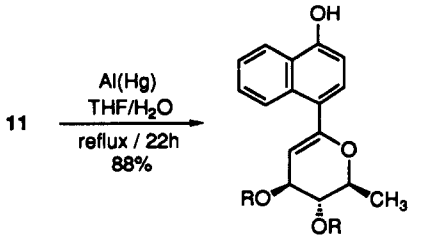


13



14 **15**

A more direct route proved feasible for the reductive aromatization of naphthoquinol **11**. The successful procedure involved treatment with aluminum/mercury amalgam[9] in aqueous THF at 50 °C for approximately 2 h to afford naphthol glycal **16** in high yield.

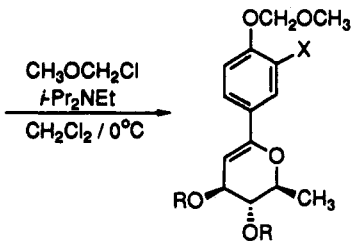


16

(8) Depew, M. C.; Wan, J. K. S. In *The Chemistry of Quinonoid Compounds*; Patai, S., Rappaport, Z., Eds.; John Wiley and Sons: New York, 1988; Vol. 2, Part 2, p 1004.
(9) Stahly, G. P.; Bell, D. P. *J. Org. Chem.* **1989**, *54*, 2873.

The aluminum amalgam procedure was also applicable to the reduction of benzoquinol glycals 8. Yields of *C*-aryl glycals 9 were comparable for the dithionite and aluminum amalgam procedures.

Although the direct preparation of *p*-hydroxyaryl glycals may be considered the goal of this work, easy access to these compounds suggests that a variety of protected phenols might be available for further manipulation. We are especially interested in the possibility that the chromium carbene benzannulation protocol, demonstrated in the synthesis of 1-*O*-methyldefucogilvocarcin V,[10] might convert glycosylated substrates to gilvocarcins in a reasonably direct fashion. In the context of this strategy, it is gratifying to note that phenols **9a** and **9b** were readily protected, under standard conditions, as the corresponding MOM phenyl ethers **17a** and **17b**.



17a X = H; R = TBDMS
b X = Br; R = TBDMS

The methodology described above provides excellent yields of regiospecifically substituted *C*-aryl glycals by an extremely short and easy-to-perform sequence. We are confident that it will be broadly applied in the *C*-aryl glycoside field.

Experimental Section[11]

Quinol 2a. To a solution of 401 mg (4.78 mmol) of dihydropyran in 2.0 mL of THF and 10.0 mL of hexane at −78 °C was added 3.40 mL (5.98 mmol) of *t*-BuLi (1.7 M in pentane). After being stirred for 5 min the solution was warmed to 0 °C and stirred an additional 30 min. The resulting solution of 2-lithiodihydropyran was recooled to −78 °C and added by cannula to a −100 °C solution of 659 mg (5.98 mmol) of *p*-benzoquinone (**7a**) in 6 mL of THF and 4 mL of hexane. The green reaction mixture was stirred for 5 h and then poured into 35 mL of saturated $NaHCO_3$ and extracted with CH_2Cl_2 (5 × 30 mL). The organic extracts were passed through a plug of Florisil (×2) and dried ($MgSO_4$). Column chromatography (1:2 EtOAc/hexanes) left 551 mg (60%) of quinol **2a** as a white solid: mp 86–88 °C dec; ^1H NMR ($CDCl_3$) δ 1.83 (m, 2 H), 2.05 (m, 2 H), 3.07 (s, 1 H), 4.04 (m, 2 H), 4.98 (t, *J* = 3.8 Hz, 1 H), 6.21 (d, *J* = 10.1 Hz, 2 H), 6.88 (d, *J* = 10.1 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 185.0, 142.3, 139.6, 124.5, 124.1, 95.3, 68.6, 50.9, 27.7; IR (CCl_4) 3358, 1668 cm^{-1}; HRMS calcd 192.2165, found 192.2183.

Phenol 5a. To a solution of 192 mg (1.0 mmol) of quinol **2a** in 3 mL of THF and 1 mL of H_2O was added 348 mg (2.0 mmol) of $Na_2S_2O_4$. After being stirred at 24 °C for 3 h, the mixture was diluted with ether (10 mL) and the organic solution was dried (Na_2SO_4). Column chromatography (1:2 EtOAc/hexanes) gave 146 mg (83%) of phenol **5a** as a colorless oil: ^1H NMR ($CDCl_3$) δ 7.43 (d, *J* = 8.8 Hz, 2 H), 6.76 (d, *J* = 8.8 Hz, 2 H), 6.05 (bs, 1 H), 5.23 (t, *J* = 3.9 Hz, 1 H), 4.18 (t, *J* = 5.1 Hz, 2 H), 2.19 (m, 2 H), 1.89 (m, 2 H); IR (neat) 3428, 1649 cm^{-1}; HRMS calcd 176.2216, found 176.2231.

Bromoquinol 2b. To a solution of 1.95 g (23.2 mmol) of dihydropyran in 7 mL of THF at −78 °C was added 10.9 mL (18.6 mmol) of *t*-BuLi (1.7 M in pentane). After 5 min the solution was warmed to 0 °C and stirred for 30 min. The yellow solution of 2-lithiodihydropyran was recooled to −78 °C and transferred by cannula to a −78 °C solution of 3.46 g (18.5 mmol) of bromobenzoquinone (**7b**) in 30 mL of THF. After being stirred for 5 h, the reaction was quenched with 10 mL of H_2O and diluted with 150 mL of ether. The organic phase was washed with H_2O (3 × 20 mL), 5% NaOH (2 × 15 mL), H_2O (30 mL), and then brine (30 mL). Drying (Na_2SO_4) and column chromatography (2:3 EtOAc/hexanes) left 2.9 g (60%) of quinol **2b** as a yellow oil: ^1H NMR ($CDCl_3$) δ 7.32 (d, *J* = 2.8 Hz, 1 H), 6.88 (dd, *J* = 2.8, 10.0 Hz, 1 H), 6.30 (d, *J* = 10.0 Hz, 1 H), 5.00 (t, *J* = 3.9 Hz, 1 H), 4.08 (t, *J* = 5.2 Hz, 2 H), 3.51 (s, 1 H), 2.03 (m, 2 H), 1.84 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 178.3, 148.9, 148.6, 127.1, 126.7, 123.9, 98.5, 71.7, 67.2, 67.1, 21.8, 19.8; IR (neat) 3430, 1670 cm^{-1}; HRMS calcd for ^{81}Br 272.1239, found 272.1245.

Bromophenol 5b. To a solution of 2.00 g (7.40 mmol) of bromoquinol **2b** in 48 mL of THF and 16 mL of H_2O was added 2.94 g (14.4 mmol) of $Na_2S_2O_4$. After being stirred for 2 h, the reaction mixture was washed with ether (2 × 50 mL), dried (Na_2SO_4), and chromatographed (2:3 EtOAc/hexanes) to afford 1.47 g (78%) of phenol **5b** as a yellow oil: ^1H NMR ($CDCl_3$) δ 7.66 (d, *J* = 2.1 Hz, 1 H), 7.35 (dd, *J* = 2.1, 8.5 Hz, 1 H), 6.90 (d, *J* = 8.5 Hz, 1 H), 5.65 (s, 1 H), 5.21 (t, *J* = 3.8 Hz, 1 H), 4.15 (t, *J* = 5.0 Hz, 2 H), 2.21 (m, 2 H), 1.89 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 156.6, 132.9, 129.6, 128.1, 125.2, 115.5, 114.1, 96.6, 62.3, 22.3, 20.7; IR (neat) 3377, 1651 cm^{-1}; HRMS calcd for ^{81}Br 256.1290, found 256.1280.

Quinol Glycal 8a. To a solution of 970 mg (2.71 mmol) of glycal **6** in 3 mL of THF at −78 °C was added 3.12 mL (5.42 mmol) of *t*-BuLi (1.7 M in pentane), and the solution was warmed to 0 °C and stirred at this temperature for 105 min. The mixture was then recooled to −100 °C and added via cannula to a −78 °C solution of 642 mg (5.92 mmol) of sublimed **7a** in 25 mL of THF. After 8 h, the solution was quenched with 100 mL of water and was extracted with ether (4 × 100 mL). The organic phases were washed with 0.5% NaOH (3 × 20 mL), H_2O (2 × 25 mL), and then brine (50 mL). Drying ($MgSO_4$) and chromatography (3:7 EtOAc/hexanes) gave 1.11 g (91%) of quinol **8a** as a colorless oil: ^1H NMR ($CDCl_3$) δ 6.82 (m, 2 H), 6.15 (m 2 H), 4.92 (dd, *J* = 0.8, 4.0 Hz, 1 H), 4.05 (m, 1 H), 3.99 (m, 1 H), 3.55 (m, 1 H), 3.13 (s, 1 H), 1.25 (d, *J* = 6.8 Hz, 3 H), 0.85 ("s", 18 H), 0.08 ("s", 12 H); ^{13}C NMR ($CDCl_3$) δ 185.4, 150.1, 148.1, 147.8, 128.6, 128.2, 98.6, 76.4, 73.6, 69.1, 68.5, 25.8, 25.7, 18.0, 17.9, 16.3, −4.0, −4.22, −4.25, −4.5; IR (neat) 3430, 1667 cm^{-1}; HRMS calcd 466.2570, found 466.2582.

Phenol Glycal 9a. To a solution of 46.5 mg (0.10 mmol) of quinol **8a** in 2.5 mL of THF and 1.0 mL of H_2O was added 52 mg (0.30 mmol) of $Na_2S_2O_4$. The mixture was stirred at room temperature for 3 h, and then the solvent was evaporated. Column chromatography (1:2 EtOAc/hexanes) left 37.7 mg (84%) of phenol **9a** as a colorless oil: ^1H NMR ($CDCl_3$) δ 7.42 (d, *J* = 8.7 Hz, 2 H), 6.76 (d, *J* = 8.7 Hz, 2 H), 5.08 (d, *J* = 3.3 Hz, 1 H), 4.88 (bs, 1 H), 4.27 (m, 1 H), 4.05 (m, 1 H), 3.59 (m, 1 H), 1.40 (d, *J* = 6.6 Hz, 3 H), 0.92 (s, 9 H), 0.89 (s, 9 H), 0.11 (s, 3 H), 0.10 (s, 3 H), 0.09 (s, 3 H), 0.06 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 156.1, 150.9, 127.9, 126.7, 115.0, 97.8, 75.6, 75.2, 71.1, 25.9, 25.8, 25.7, 25.6, 17.3, −3.5, −3.6, −3.9, −4.2; IR (neat) 3429, 1650 cm^{-1}; HRMS calcd 450.2621, found 450.2640.

Bromoquinol Glycal 8b. To a solution of 622 mg (1.74 mmol) of the silylated rhamnal **6** in 1 mL of THF at −78 °C was added 2.00 mL (3.74 mmol) of *t*-BuLi (1.7 M in pentane), and the solution was warmed to 0 °C and stirred at this temperature for 2 h. The mixture was then recooled to −100 °C and added via cannula to a −78 °C solution of 711 mg (3.82 mmol) of **7b** in 25 mL of THF. After 4 h, the solution was quenched with 100 mL of water and was extracted with ether (4 × 100 mL). The organic phases were washed with 1% NaOH (3 × 20 mL), H_2O (2 × 25 mL), and then brine (50 mL). Drying ($MgSO_4$) and chromatography (3:7 EtOAc/hexanes) left 741 mg (78%) of phenol **8b** as a colorless oil: ^1H NMR ($CDCl_3$) δ 7.46 (dd, *J* = 2.7, 15.7 Hz, 1 H), 7.04 (m, 1 H), 6.49 (m, 1 H), 5.17 (dd, *J* = 4.0, 10.7 Hz, 1 H), 4.29 (m, 1 H),

(10) Parker, K. A.; Coburn, C. A. *J. Org. Chem.* **1991**, *56*, 1666.

(11) Solvents were dried and purified by standard methods before use. Ether refers to diethyl ether. Flash chromatography was performed using E. Merck silica gel 60 (70–230 mesh). Each new compound was characterized by IR and ^1H NMR spectroscopy and by an elemental analysis or by a ^{13}C NMR spectrum and a high-resolution mass. ^1H NMR spectra were recorded at 400.1 MHz on a Bruker AM400WB spectrometer or at 250 MHz on a Bruker WM250 with chemical shifts reported in parts per million relative to tetramethylsilane. ^{13}C NMR spectra were recorded at 100.6 MHz on the Bruker AM 400WB spectrometer with chemical shifts reported in parts per million relative to deuteriochloroform as an internal standard. IR spectra were recorded as indicated on a Perkin-Elmer 1600 FT-IR spectrometer. High-resolution mass spectra were recorded with a Kratos MS-80 high-resolution spectrometer under EI or CI conditions.

4.21 (m, 1 H), 3.78 (bs, 1 H), 3.43 (m, 1 H), 1.43 (d, J = 6.8 Hz, 3 H), 1.04 ("s", 18 H), 0.25 ("s", 12 H); ^{13}C NMR ($CDCl_3$) δ 185.7, 148.3, 132.8, 127.4, 124.6, 98.1, 76.3, 73.2, 71.1, 68.4, 25.8, 25.6, 18.0, 17.8, 16.2, -4.0, -4.2, -4.3, -4.5; IR (neat) 3433, 1668 cm^{-1}; HRMS calcd for ^{81}Br (M - H$^+$) 545.1566, found 545.1608.

Bromophenol Glycal 9b. To a solution of 54.4 mg (0.100 mmol) of quinol **8b** in 2.5 mL of THF and 1.5 mL of H_2O was added 52 mg (0.30 mmol) of $Na_2S_2O_4$. The mixture was stirred at room temperature for 5 h, and then the solvent was evaporated. Column chromatography (1:2 EtOAc/hexanes) left 45.9 mg (87%) of phenol **9b** as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 7.69 (d, J = 1.9 Hz, 1 H), 7.40 (dd, J = 1.7, 8.5 Hz, 1 H), 6.93 (d, J = 8.5 Hz, 1 H), 5.71 (bs, 1 H), 5.08 (d, J = 3.4 Hz, 1 H), 4.23 (m, 1 H), 4.07 (m, 1 H), 3.53 (m, 1 H), 1.45 (d, J = 6.6 Hz, 3 H), 0.92 (s, 9 H), 0.88 (s, 9 H), 0.12 (s, 3 H), 0.10 (s, 3 H), 0.09 (s, 3 H), 0.06 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 152.1, 133.0, 128.8, 125.9, 115.5, 110.2, 98.4, 75.6, 74.7, 70.4, 26.0, 25.8, 19.9, 19.8, 17.0, -3.7, -3.8, -4.0, -4.3; IR (neat) 3463, 1651 cm^{-1}; HRMS calcd for ^{81}Br (M - H$^+$) 529.1617, found 529.1670.

Ketone 10. To a solution of 54.4 mg (0.100 mmol) of quinol **8b** in 2.5 mL THF and 1.0 mL of H_2O was added 174 mg (1.00 mmol) of $Na_2S_2O_4$. After being stirred for 28 h at 24 °C, the mixture was diluted with ether and the layers were separated. The organic phase was dried (Na_2SO_4), and after evaporation and chromatography (1:2 EtOAc/hexanes) 42.1 mg (90%) of ketone **10** was recovered as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 7.99 (d, J = 8.9 Hz, 1 H), 6.94 (d, J = 8.9 Hz, 1 H), 4.60 (m, 1 H), 4.25 (bs, 1 H), 3.95 (m, 1 H), 3.46 (dd, J = 4.1, 8.5 Hz, 1 H), 3.36 (m, 1 H), 3.06 (dd, J = 1.8, 16.0 Hz, 1 H), 1.23 (d, J = 6.1 Hz, 3 H), 0.82 (s, 9 H), 0.75 (s, 9 H), 0.16 (s, 3 H), 0.11 (s, 3 H), 0.08 (s, 3 H), -0.09 (s, 3 H); IR (neat) 3433, 1680 cm^{-1}; HRMS calcd for 468.2727, found 468.2779.

Naphthoquinol Glycal 11. To a solution of 740 mg (2.07 mmol) of **6** in 4.20 mL of dry THF at -78 °C was added 2.38 mL (4.05 mmol, 2.00 equiv) of t-BuLi (1.7 M in pentane). The solution was warmed to 0 °C, stirred at this temperature for 2 h, and then recooled to -78 °C and added to a -78 °C solution of 616 mg (3.90 mmol) of 1,4-naphthoquinone in 10 mL of THF. After being warmed to room temperature over 23 h, the solution was diluted with 30 mL of ether and quenched with 10 mL of H_2O. The aqueous phase was extracted with ether (5 × 10 mL), dried (Na_2SO_4), and chromatographed to leave 800 mg (75%) of glycal **11** as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 8.05 (dd, J = 0.7, 7.2 Hz, 1 H), 7.61 (m, 1 H), 7.55 (m, 1 H), 7.36 (m, 1 H), 6.91 (dd, J = 6.5, 10.2 Hz, 1 H), 6.36 (dd, J = 5.2, 10.2 Hz, 1 H), 4.91 (d, J = 3.7 Hz, 1 H), 3.99 (m, 2 H), 3.50 (m, 1 H), 3.05 (s, 1 H), 1.23 (d, J = 6.9 Hz, 3 H), 0.85 (s, 9 H), 0.74 (s, 9 H), -0.03-0.09 (4 singlets); ^{13}C NMR ($CDCl_3$) δ 184.6, 152.5, 149.3, 143.5, 132.8, 130.6, 128.3, 128.2, 126.1, 98.3, 76.1, 73.4, 70.4, 68.2, 25.6, 25.5, 17.9, 17.8, 16.0, -4.1, -4.2, -4.3, -4.5; IR (neat) 3432, 1669, 1559, 1471, 1298, 1252, 1108 cm^{-1}; HRMS calcd for (M - H$^+$) 499.2700, found 499.2789.

Unsaturated Lactone 12. To a solution of 65.0 mg (0.126 mmol) of naphthoquinol **11** in 1.0 mL of dioxane and 1.0 mL of H_2O was added 516 mg (2.52 mmol, 20.0 equiv) of $Na_2S_2O_4$. After being stirred for 21 h at 24 °C under N_2, the mixture was diluted with ether and the layers were separated. The organic phase was dried (Na_2SO_4) and after evaporation and chromatography (1:2 EtOAc/hexanes) gave 20.5 mg (67%) of lactone **12** as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 6.72 (dd, J = 1.7, 9.9 Hz, 1 H), 5.92 (dd, J = 1.9, 9.9 Hz, 1 H), 4.28 (m, 2 H), 1.46 (d, J = 5.9 Hz, 3 H), 0.93 (s, 9 H), 0.15 (s, 3 H), 0.14 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 150.0, 119.7, 78.9, 68.7, 25.6, 25.5, 18.0, -4.5, -4.9; IR (neat) 1738 cm^{-1}; HRMS calcd 242.1338, found 242.1342.

Naphthalene 15. To a solution of 10.0 g (32.7 mmol) of naphthoquinol **13** in 300 mL of acetonitrile was added 18 g (83 mmol) of di-*tert*-butyl dicarbonate and 500 mg of DMAP (4 mmol). The solution was stirred at room temperature under N_2 for 18 h and then diluted with 300 mL of ethyl acetate and washed with water (2 × 100 mL). At this point the enol imine **14** could be isolated and purified by chromatography (^{1}H NMR ($CDCl_3$) δ 7.3-7.5 (m, 4 H), 6.61 (s, 1 H), 5.90 (m, 1 H), 5.50 (m, 1 H), 5.20 (d, J = 17.0, 1 H), 5.10 (d, J = 10.2, 1 H), 4.93 (d, J = 10.2, 1 H), 4.84 (d, J = 16.9, 1 H), 4.25 (m, 2 H), 2.80 (m, 2 H), 1.55 (s, 9 H), 1.34 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 164.7, 152.6, 150.8, 149.7, 140.9, 135.0, 130.1, 129.6, 127.2, 126.9, 124.5, 122.3, 119.2, 115.4, 104.5, 83.9, 82.0, 81.3, 53.1, 49.1, 27.34, 27.32), but in practice the solution was concentrated to approximately 100 mL and diluted with water (100 mL), and then 36 g (210 mmol) of sodium dithionite was added. The mixture was thoroughly degassed with nitrogen and stirred for 24 h at room temperature. The organic layer was separated, washed with water (2 × 50 mL) and brine, dried (Na_2SO_4), and chromatographed (10% ethyl acetate in hexane) to give 9.3 g (73%) of naphthalene **15** as a pale yellow oil which crystallized upon standing to give a yellow solid: mp 108-109 °C (hexane); ^{1}H NMR ($CDCl_3$) δ 7.81 (d, J = 9.0 Hz, 2 H), 7.3-7.5 (m, 7 H), 6.95 (s, 1 H), 6.00 (m, 1 H), 5.05 (d, J = 10.2 Hz, 1 H), 4.96 (d, J = 17.4 Hz, 1 H), 4.45 (d, J = 4.7 Hz, 2 H), 4.27 (bs, 1 H), 3.66 (d, J = 5.4 Hz, 2 H), 1.57 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 152.1, 146.9, 143.5, 139.2, 134.8, 133.9, 128.7, 127.4, 127.3, 126.9, 122.5, 122.1, 121.5, 120.9, 115.8, 112.2, 106.9, 83.4, 48.4, 30.1, 27.7; IR (mull) 3458, 1752, 1627 cm^{-1}; HRMS calcd 389.1991, found 389.1999. Anal. Calcd for $C_{25}H_{27}NO_3$: C, 77.09; H, 7.03; N, 3.58. Found: C, 77.14; H, 7.03; N, 3.58.

Naphthol Glycal 16. To a solution of 100 mg (0.19 mmol) of naphthoquinol **11** in 1.8 mL of THF and 0.2 mL of H_2O was added 30 mg (1.1 mmol, 5.8 equiv) of amalgamated aluminum foil (formed by immersing in 2% aqueous $HgCl_2$, washing with EtOH, then Et_2O),[9] and the whole was heated at reflux for 2 h. The reaction mixture was filtered through Florisil, dried ($MgSO_4$), and evaporated to leave 85 mg (88%) of naphthol **16**: ^{1}H NMR ($CDCl_3$) δ 8.15 (m, 2 H), 7.50 (m, 2 H), 7.34 (d, J = 7.7 Hz, 1 H), 6.76 (d, J = 7.7 Hz, 1 H), 5.31 (s, 1 H), 4.95 (d, J = 3.8 Hz, 1 H), 4.25 (m, 2 H), 3.75 (m, 1 H), 1.50 (d, J = 6.8 Hz, 3 H), 0.95 (s, 9 H), 0.89 (s, 9 H), 0.17-0.05 (6 singlets); ^{13}C NMR ($CDCl_3$) δ 152.1, 151.9, 132.7, 127.7, 126.7, 126.6, 125.9, 125.3, 125.1, 121.6, 107.7, 102.7, 75.9, 74.2, 69.8, 25.7, 25.6, 18.1, 18.0, 17.1, -3.8, -4.00, -4.06, -4.3; IR (CCl_4) 3369, 1672 cm^{-1}; HRMS calcd 484.2828, found 484.2834.

Protected Glycal 17a. To a solution of 272 mg (0.606 mmol) of phenol **9a** in 10 mL of CH_2Cl_2 was added 156 mg (0.21 mL, 1.21 mmol) of Hunig's base and 80 mg (1.0 mmol) of chloromethyl methyl ether at 0 °C. The mixture was stirred for 24 h, diluted with 10 mL of CH_2Cl_2, and washed with H_2O (2 mL), $NaHCO_3$ (2 × 3 mL), and then brine (5 mL). Drying (Na_2SO_4) and chromatography (1:4 EtOAc/hexanes) gave 254 mg (85%) of glycal **17a** as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 7.48 (d, J = 8.9 Hz, 2 H), 6.95 (d, J = 8.9 Hz, 2 H), 5.16 (s, 2 H), 5.09 (d, J = 3.3 Hz, 1 H), 4.25 (m, 1 H), 4.05 (t, J = 6.7 Hz, 1 H), 3.59 (m, 1 H), 3.46 (s, 3 H), 1.38 (d, J = 6.6 Hz, 3 H), 0.91 (s, 9 H), 0.89 (s, 9 H), 0.12 (s, 3 H), 0.11 (s, 3 H), 0.09 (s, 3 H), 0.06 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 157.4, 150.8, 129.1, 126.5, 116.2, 115.8, 98.1, 94.3, 75.6, 75.1, 55.9, 29.3, 26.1, 25.9, 18.2, 18.0, 17.3, -3.5, -3.6, -3.9, -4.2; IR (neat) 1652, 1510 cm^{-1}; HRMS calcd for M - H$^+$ 493.2805, found 493.2779.

Protected Bromo Glycal 17b. To a solution of 52.9 mg (0.10 mmol) of quinol **9b** in 2 mL of CH_2Cl_2 at 0 °C and 30.8 mg (0.287 mmol) of diisopropylethylamine was added 11.8 mg (0.142 mmol) of MOMCl. The solution was stirred at 0 °C, diluted with 1 mL of CH_2Cl_2, and washed with H_2O (0.5 mL), $NaHCO_3$ (2 × 0.5 mL), and then brine (1 mL). Drying (Na_2SO_4) and chromatography (1:4 EtOAc/hexanes) left 39.3 mg (85%) of glycal **17b** as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 7.77 (d, J = 2.2 Hz, 1 H), 7.45 (dd, J = 2.2, 8.7 Hz, 1 H), 7.09 (d, J = 8.7 Hz, 1 H), 5.25 (s, 2 H), 5.11 (d, J = 3.4 Hz, 1 H), 4.22 (m, 1 H), 4.10 (t, J = 6.7 Hz, 1 H), 3.59 (m, 1 H), 3.46 (s, 3 H), 1.40 (d, J = 6.6 Hz, 3 H), 0.91 (s, 9 H), 0.89 (s, 9 H), 0.12 (s, 3 H), 0.11 (s, 3 H), 0.09 (s, 3 H), 0.06 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 153.0, 137.7, 130.8, 125.8, 120.7, 115.5, 99.3, 95.0, 78.1, 71.4, 69.9, 56.5, 29.1, 26.2, 26.0, 18.1, 18.0, 15.0, -2.7, -3.1, -3.9, -4.0; IR (neat) 2955, 2856, 1650, 1510, 1471 cm^{-1}; HRMS calcd for ^{81}Br (M - H$^+$) 573.1881, found 573.1801.

Acknowledgment. Work carried out at Brown University was supported by the National Institutes of Health (Grant No. CA50720). C.A.C. is the recipient of the Rohm and Haas Company Graduate Fellowship administered by the Organic Division of the American Chemical Society.

Supplementary Material Available: ^{1}H NMR spectra of **2, 5, 8-12,** and **14-17** (16 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.