

3 h and then quenched by addition of absolute methanol (2 mL) at room temperature. After centrifugation of the precipitate, the solvents were evaporated. The crude product was purified by column chromatography using ether/petroleum ether/triethylamine (1/9/0.1) as eluent to give **9b** (yield 0.44 g, 80%) as a 50:50 mixture of 1*E*,3*E* and 1*Z*,3*E* isomers: IR (neat) 1620 cm^{-1} ; MS (CI, CH_4) m/z 262 ($M + 1$, 100); HRMS calcd for $\text{C}_{15}\text{H}_{15}\text{NOS}$ m/z 261.1187, found 261.1194; ^1H NMR (200 MHz, CDCl_3) δ (ppm) 1*E*,3*E* isomer, 1.99 (3 H, s), 2.93 (4 H, m), 3.69 (4 H, m), 5.66 (1 H, s), 5.83 (1 H, d, $J = 13.9$ Hz), 6.31 (1 H, d, $J = 13.9$ Hz), 7.1–7.3 (5 H, m); 1*Z*,3*E* isomer, 1.99 (3 H, s), 2.93 (4 H, m), 3.69 (4 H, m), 5.40 (1 H, d, $J = 13.9$ Hz), 5.89 (1 H, s), 6.22 (1 H, d, $J = 13.9$ Hz), 7.1–7.3 (5 H, m).

(1*E*,3*E*)- and (1*Z*,3*E*)-1-Morpholino-4-(phenylthio)buta-1,3-dienes (**9a**). The procedure was similar to that for **9b** starting from 0.4 g of **4a**. The yield was 0.35 g (80%) of a 53:47 crude mixture of 1*E*,3*E* and 1*Z*,3*E* isomers: IR (neat) 2950, 1625 cm^{-1} ; MS (CI, CH_4) m/z 248 ($M + 1$, 100); HRMS calcd for $\text{C}_{14}\text{H}_{17}\text{NOS}$ m/z 247.1031, found 247.1040; ^1H NMR (200 MHz, C_6D_6) δ (ppm) 1*E*,3*E* isomer, 2.31 (4 H, m), 3.20 (4 H, m), 5.05 (1 H, dd, $J = 13.4$, $J = 10.6$ Hz), 5.64 (1 H, d, $J = 13.4$ Hz), 5.95 (1 H, d, $J = 14.4$ Hz), 6.59 (1 H, dd, $J = 10.6$, $J = 14.4$ Hz), 6.8–7.4 (5 H, m); 1*Z*,3*E* isomer, 2.31 (4 H, m), 3.20 (4 H, m), 5.71–5.85 (3 H, m), 6.35 (1 H, dd, $J = 9.1$, $J = 9.1$ Hz), 6.8–7.4 (5 H, m).

Acknowledgment. We are deeply indebted to Dr. G. Plé for full 400-MHz ^1H NMR spectra and help with their analysis. We wish to thank also Mr. A. Marcual for mass spectrometry and CNRS for financial support.

Supplementary Material Available: ^1H NMR spectra for compounds **4a**, **5b**, **6b**, **7a,b**, **8b**, and **9a,b** (12 pages). Ordering information is given on any current masthead page.

Regiospecific Synthesis of Hydroxyquinones and Related Compounds from 3-*tert*-Butoxycyclobutene-1,2-dione

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Reported here is the synthesis of 3-*tert*-butoxycyclobutene-1,2-dione, **2**, and its utility as a reagent for the regiospecific synthesis of substituted hydroxyquinones. This cyclobutenedione was readily obtained in 72% yield upon treatment of di-*tert*-butyl squarate, **1**, with lithium tri-*tert*-butoxyaluminumhydride followed by hydrolysis with aqueous HCl.^{1,2}

The cyclobutenedione **2** undergoes facile regiospecific addition of aryl- or alkenyllithium reagents to the more electrophilic carbonyl group at position 2 to give 4-aryl(or alkenyl)-3-*tert*-butoxy-4-hydroxycyclobutenones **3** as outlined in Scheme II. Thermolysis (refluxing *p*-xylene or toluene, 15–60 min) of these adducts followed by oxidation of the resulting hydroquinone **6** (Ag_2O , K_2CO_3) provides the quinones **7a–f** in good overall yields (Table I). These ring expansions provide further examples of the synthetic scope of the known rearrangements of 4-aryl(or alkenyl)cyclobutenones to hydroquinones. The rearrangements are envisaged to involve initial electrocyclic ring opening to the conjugated ketenes **4**, which undergo

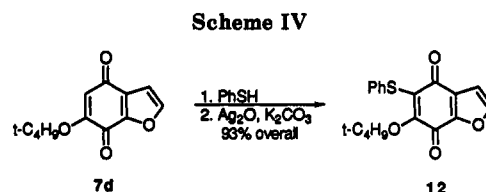
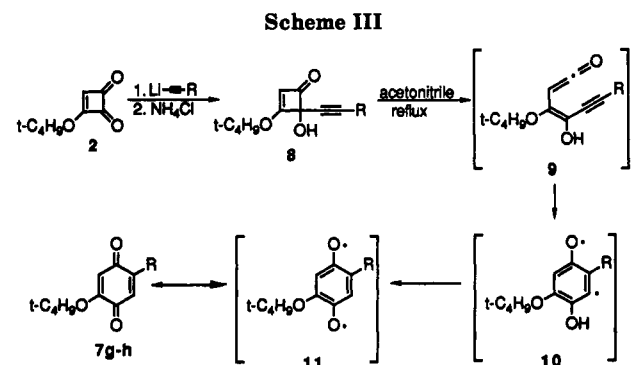
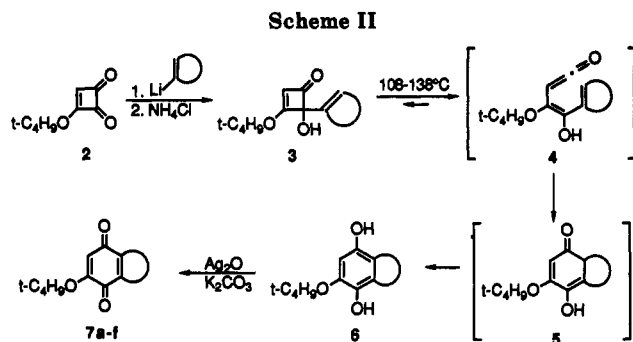
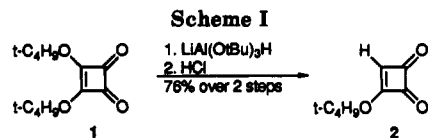


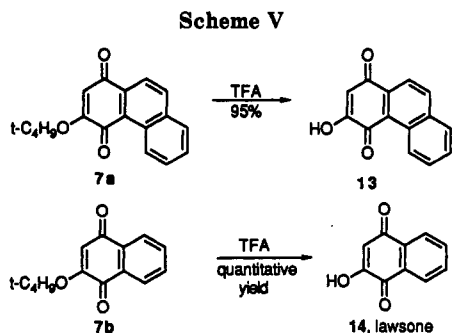
Table I *tert*-Butoxy Quinones

entry	lithium reagent	R	quinone	% yield from 2
7a				48
7b		H		63
7c		CH ₃		48
7d				53
7e		CH ₃		66
7f		n-Bu		58
7g		CH ₃		63
7h		n-Bu		56

(1) The 3-isopropoxycyclobutene-1,2-dione has previously been prepared in an analogous fashion: Liebeskind, L. S.; Fengl, R. W.; Wirtz, K. R.; Shawe, T. T. *J. Org. Chem.* 1988, 53, 2482.

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ring closure to **5** and final tautomerization to the hydroquinones **6**.³



Compound **2** was also employed for the synthesis and similar ring expansion of 4-alkynyl-3-*tert*-butoxy-4-hydroxycyclobutenones as illustrated in Scheme III.⁴ Addition of the appropriate alkynyllithium reagent proceeded smoothly to give the desired cyclobutenones **8** in excellent (91–96%) yields. Thermolysis of **8** in refluxing acetonitrile (0.5–1 h) provided quinones **7g–h**. The mechanism of this thermal ring expansion has previously been shown to involve formation of the ketene **9**, which undergoes ring closure to the diradical **10** and subsequent hydrogen transfer to give the quinones **7g–h**.

A transformation illustrating the potential utility of these ring expansions is outlined in Scheme IV. Specifically, the conversion of **7d** to **12** demonstrates the regiocontrol in synthesizing highly substituted annulated quinones by this methodology in that no product arising from addition at the carbon bearing the bulky *tert*-butoxy group is isolated.

Illustrated in Scheme V are two examples of the deprotection of a *tert*-butoxy quinone, a transformation recently reported to be a facile route to hydroxyquinones.^{5,6} Addition of trifluoroacetic acid to 2-*tert*-butoxy-1,4-phenanthrene-9,10-dione, **7a**, provided 2-hydroxy-1,4-phenanthrene-9,10-dione, **13**, in excellent yield (95%). Similarly, deprotection of **7b** afforded the natural product lawsone, **14**, a simple hydroxyquinone identified as the coloring agent in henna dyes.⁷

In conclusion, a synthetically useful method for the regioselective synthesis of substituted hydroxybenzoquinones and annulated derivatives is reported.

Experimental Section⁸

General. All air- or water-sensitive reactions were carried out under a slight positive pressure of Ar. THF was distilled from sodium (benzophenone indicator). *p*-Xylene, toluene, and acetonitrile were distilled from CaH₂. Unless specified as dry, the solvents were of unpurified reagent grade. Removal of solvents was accomplished on a rotary evaporator at 20–30 Torr. All reactions were followed by TLC using E. Merck precoated sheets of silica gel 60 F₂₅₄. Flash column chromatography was performed

using E. Merck silica gel 60 (230–400 mesh). Melting points are not corrected. ¹H NMR spectra were recorded at 250 or 500 MHz; ¹³C NMR data were collected at 500 MHz.

3-*tert*-Butoxy-3-cyclobutene-1,2-dione (2). Di-*tert*-butyl squarate (**1**) (1.0 g, 4.4 mmol) was dissolved in dry THF (40 mL) and cooled to –5 °C under Ar. LiAl(OC(CH₃)₃)₃H (5.5 mL of a 1.0 M solution in THF, 5.5 mmol) was added. After 30 min the reaction was poured into a saturated solution of potassium sodium tartrate (20 mL) and ether (20 mL). The aqueous layer was extracted with ether (2 × 20 mL). The organic layers were combined, filtered through a short column of silica gel, and evaporated to give the intermediate alcohol as a light yellow oil, which was used without further purification.

The crude alcohol was placed in CH₂Cl₂ (10 mL), and concd HCl (4 drops) was added. After being stirred 30 min the reaction mixture was diluted with CH₂Cl₂ (20 mL), dried over MgSO₄, filtered, and evaporated to give a light yellow oil, which was purified by column chromatography on silica gel (6:1 hexane/ethyl acetate) to give **2** (0.49 g, 72% from **1**) as light yellow needles that decomposed slowly at rt: ¹H NMR (CDCl₃) δ 8.53 (s, 1 H), 1.52 (s, 9 H); ¹³C NMR (CDCl₃) δ 199.4, 195.9, 193.7, 164.9, 88.7, 27.9.

General Procedure for the Synthesis of *tert*-Butoxy Quinones, 7a–f. **2-*tert*-Butoxy-1,4-phenanthrene-9,10-dione (7a).** To a solution of 2-bromonaphthalene (180 μL, 1.3 mmol) in dry THF (8 mL), cooled to –78 °C under Ar, was added *n*-BuLi (0.74 mL of a 1.6 M solution in hexane, 1.2 mmol). After stirring for 30 min, the anion was added via cannula to a –78 °C solution of dione **2** (170 mg, 1.1 mmol) in dry THF (30 mL). After stirring another 30 min, the reaction mixture was poured into NH₄Cl (10%, 20 mL). The aqueous layer was extracted with ethyl acetate (2 × 30 mL). The organic layers were combined, washed with brine, dried over MgSO₄, filtered, and evaporated. The resulting alcohol was purified by flash column chromatography on silica gel (2:1 hexane/ethyl acetate) to give a white powder, which was used without characterization.

The alcohol was dissolved in dry *p*-xylene (80 mL) and heated at reflux under Ar for 25 min. Upon cooling to rt Ag₂O (550 mg, 2.4 mmol) and K₂CO₃ (330 mg, 2.4 mmol) were added and the suspension was stirred at rt for 1.75 h. The reaction mixture was then filtered through Celite and evaporated to a bright yellow oil. The oil was purified by flash column chromatography on silica gel (10:1 hexane/ethyl acetate) to give **7a** (140 mg, 48% from dione **2**) as a bright yellow powder: IR (CHCl₃, cm⁻¹) 1670, 1640, 1610; ¹H NMR (CDCl₃) δ 6.29 (s, 1 H), 1.63 (s, 9 H); ¹³C NMR (CDCl₃) δ 185.7, 183.5, 157.7, 136.1, 135.2, 132.2, 130.0, 129.9, 128.7, 128.2, 127.6, 126.5, 121.6, 110.8, 82.8, 27.9.

2-*tert*-Butoxy-1,4-naphthoquinone (7b). Phenyllithium addition to **2**, reflux in *p*-xylene (30 min), and oxidation gave **7b** (160 mg, 63%) after purification by flash column chromatography on silica gel (10:1 hexane/ethyl acetate) as a bright yellow powder: IR (CHCl₃, cm⁻¹) 1686, 1680, 1645; ¹H NMR (CDCl₃) δ 6.31 (s, 1 H), 1.57 (s, 9 H); ¹³C NMR (CDCl₃) δ 185.0, 180.9, 157.1, 133.8, 133.0, 131.6, 131.2, 126.5, 125.7, 113.5, 82.6, 27.8.

2-*tert*-Butoxy-6-methyl-1,4-naphthoquinone (7c). 4-Lithiotoluene (4-bromotoluene in THF, *n*-BuLi, –78 °C) addition to **2**, reflux in *p*-xylene (30 min), followed by oxidation and purification by flash column chromatography on silica gel (10:1 hexane/ethyl acetate) provided **7c** (120 mg, 48%) as a light yellow powder: IR (CHCl₃, cm⁻¹) 1687, 1650; ¹H NMR (CDCl₃) δ 6.24 (s, 1 H), 2.42 (s, 3 H), 1.55 (s, 9 H); ¹³C NMR (CDCl₃) δ 185.4, 180.7, 157.2, 145.0, 133.6, 131.6, 129.0, 126.7, 126.1, 113.3, 82.5, 27.8, 21.8.

6-*tert*-Butoxy-4,7-benzofuranquinone (7d). 2-Lithiofuran (furan in THF, *n*-BuLi, –78 °C) addition to **2**, reflux in toluene (20 min), and oxidation gave **7d** (52 mg, 53%) after recrystallization (CH₂Cl₂/hexane) as a bright yellow powder: IR (CHCl₃, cm⁻¹) 1695, 1660; ¹H NMR (CDCl₃) δ 7.68 (s, 1 H), 6.80 (s, 1 H), 6.00 (s, 1 H), 1.55 (s, 9 H); ¹³C NMR (CDCl₃) δ 182.3, 170.5, 156.0, 149.9, 148.5, 128.7, 110.9, 108.0, 83.1, 27.7.

3-*tert*-Butoxy-5-methyl-2,5-cyclohexadiene-1,4-dione (7e). 2-Lithiopropene (2-bromopropene in THF, –78 °C, 2 equiv *t*-BuLi) addition to **2**, reflux in *p*-xylene (30 min), followed by oxidation and purification by flash column chromatography on silica gel (6:1 hexane/ethyl acetate) provided **7e** (46 mg, 66%) as a bright yellow oil: IR (CHCl₃, cm⁻¹) 1682, 1655; ¹H NMR (CDCl₃) δ 6.41 (m, 1 H), 5.94 (m, 1 H), 1.96 (s, 3 H), 1.45 (s, 9 H); ¹³C NMR (CDCl₃) δ 187.7, 183.1, 155.2, 143.7, 133.0, 110.8, 82.2, 27.6, 15.6.

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3-tert-Butoxy-5-butyl-2,5-cyclohexadiene-1,4-dione (7f). 2-Lithiohexene (2-bromohexene in THF, $-78\text{ }^{\circ}\text{C}$, 2 equiv of *t*-BuLi) addition to **2**, reflux in toluene (25 min), followed by oxidation and purification by flash column chromatography of silica gel (8:1 hexane/ethyl acetate) provided **7f** (52 mg, 58%) as a bright yellow oil: IR (CHCl_3 , cm^{-1}) 1675, 1651; $^1\text{H NMR}$ (CDCl_3 δ 6.40 (m, 1 H), 5.99 (d, $J = 2.4$ Hz, 1 H), 1.50 (s, 9 H); $^{13}\text{C NMR}$ (CDCl_3) δ 188.0, 183.0, 155.3, 147.6, 132.2, 110.7, 82.3, 29.7, 28.6, 27.7, 22.2, 13.7.

2-tert-Butoxy-5-methyl-2,5-cyclohexadiene-1,4-dione (7g). Into dry THF (3 mL), cooled to $-78\text{ }^{\circ}\text{C}$ under Ar, was condensed propyne gas for 30 s. *n*-BuLi (0.43 mL of a 1.2 M solution in hexane, 0.52 mmol) was added, and the resulting solution was stirred for 30 min. The anion was then added via cannula to a $-78\text{ }^{\circ}\text{C}$ solution of dione **2** (66 mg, 0.43 mmol) in dry THF (12 mL). After stirring another 30 min the solution was poured into NH_4Cl (10%, 20 mL). The aqueous layer was extracted with ethyl acetate (2×30 mL), and the organic layers were combined, washed with brine, dried over MgSO_4 , filtered, and evaporated to a light yellow oil (81 mg, 96%). The alcohol was unstable at rt, but the following spectroscopic data were obtained: IR (CHCl_3 , cm^{-1}) 1760, 1567; $^1\text{H NMR}$ (CDCl_3) δ 5.26 (s, 1 H), 1.89 (s, 3 H), 1.54 (s, 9 H).

The alcohol in dry acetonitrile (40 mL) was heated at reflux under Ar for 30 min. Upon cooling and evaporation of the solvent the quinone was purified by flash column chromatography on silica gel (4:1 hexane/ethyl acetate) to yield **7g** (53 mg, 66%) as bright yellow plates: IR (CHCl_3 , cm^{-1}) 1678, 1652; $^1\text{H NMR}$ (CDCl_3) δ 6.51 (q, $J = 1.5$ Hz, 1 H), 6.06 (s, 1 H), 2.01 (d, $J = 1.5$ Hz, 3 H), 1.52 (s, 9 H); $^{13}\text{C NMR}$ (CDCl_3) δ 188.1, 183.2, 155.3, 145.9, 131.7, 111.3, 82.5, 27.8, 15.6.

2-tert-Butoxy-5-butyl-2,5-cyclohexadiene-1,4-dione (7h). The preceding procedure was followed using 1-lithiohexyne (1-hexyne, $-78\text{ }^{\circ}\text{C}$, *n*-BuLi), which gave the intermediate alcohol (91%) as a white solid that was unstable at rt: $^1\text{H NMR}$ (CDCl_3) δ 5.25 (s, 1 H), 1.52 (s, 9 H); $^{13}\text{C NMR}$ (CDCl_3) δ 187.0, 181.9, 113.4, 90.8, 86.4, 85.3, 73.9, 30.2, 27.4, 21.8, 18.6, 13.5.

The alcohol was heated at reflux in acetonitrile for 1 h under Ar and purified as above to yield **7h** as a bright yellow solid (53 mg, 61%): IR (CHCl_3 , cm^{-1}) 1672, 1646; $^1\text{H NMR}$ (CDCl_3) δ 6.45 (t, $J = 1.4$ Hz, 1 H), 6.04 (s, 1 H), 1.51 (s, 9 H); $^{13}\text{C NMR}$ (CDCl_3) δ 187.9, 183.4, 155.1, 149.7, 130.7, 111.4, 82.4, 29.9, 28.5, 27.8, 22.4, 13.8.

6-tert-Butoxy-5-(phenylthio)-4,7-benzofuranquinone (12). Quinone **7d** (9.3 mg, 0.042 mmol) was placed in dry THF/ethanol (1:1, 1 mL) under Ar. Thiophenol (9 μL , 0.084 mmol) was added, and the reaction mixture was allowed to stir for 30 min. After evaporation of the solvent the yellow oil was dissolved in benzene (2 mL), and Ag_2O (39 mg, 0.17 mmol) and anhydrous K_2CO_3 (23 mg, 0.17 mmol) were added. The suspension was stirred for 4 h at rt, filtered through Celite, and evaporated. The crude product was eluted through a column of silica gel (5:1 hexane/acetone) to give **12** (13 mg, 93%) as a dark red oil: IR (CHCl_3 , cm^{-1}) 1675; $^1\text{H NMR}$ (CDCl_3) δ 6.81 (d, $J = 1.8$ Hz, 1 H), 1.53 (s, 9 H); $^{13}\text{C NMR}$ (CDCl_3) δ 178.0, 171.0, 158.0, 148.5, 135.5, 134.3, 130.3, 129.0, 128.9, 127.5, 127.1, 127.0, 108.8, 29.6.

2-Hydroxy-1,4-phenanthrenedione (13). To trifluoroacetic acid (4 mL), cooled to $0\text{ }^{\circ}\text{C}$, was added quinone **7a** (34 mg, 0.12 mmol). The resulting yellow solution was stirred for 15 min at $0\text{ }^{\circ}\text{C}$, during which time the solution turned orange. The acid was evaporated with toluene (2×5 mL), and the orange powder was recrystallized (acetone/hexane) to yield **13** as an orange powder (26 mg, 95%): IR (acetone- d_6 , cm^{-1}) 1630, 1585; $^1\text{H NMR}$ (acetone- d_6) δ 6.37 (s, 1 H), 3.05 (bs, 1 H, exchangeable with D_2O); $^{13}\text{C NMR}$ (acetone- d_6) δ 185.3, 184.3, 159.0, 136.4 (2), 133.7, 130.6, 130.1, 129.4, 128.6, 127.2, 125.1, 122.0, 108.0.

Lawson (14). Lawson was prepared from **7b** as described above to provide **14** (20 mg, quant. yield) as a bright yellow solid identical with the natural product:^{1a} IR (CH_2Cl_2 , cm^{-1}) 1658, 1595; $^1\text{H NMR}$ (acetone- d_6) δ 6.23 (s, 1 H), 3.08 (bs, 1 H); $^{13}\text{C NMR}$ (CDCl_3) δ 183.3, 180.2, 157.2, 133.3, 131.8, 131.3, 129.2, 124.7, 124.5, 109.5.

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assistance in obtaining mass spectral data.

Supplementary Material Available: Full experimental section and ^{13}C and/or ^1H NMR spectra for compounds **2**, **7a-h**, **8g**, **8h**, **11-14** (33 pages). Ordering information is given on any current masthead page.

A Remarkable Short Synthesis of Optically Active Mevinic Acid Analogues by Biocatalytic Lactonization of *syn*-3,5-Dihydroxy Esters¹

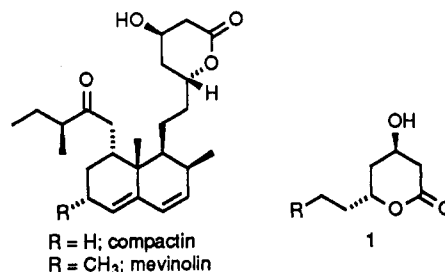
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Since the discovery of compactin and mevinolin² as potent inhibitors of HMG-CoA reductase, many asymmetric or racemic synthetic approaches to these compounds have appeared.³ Despite its rather simple structure, the lactone moiety of the mevinic acids has proved to be essential for the biological activity of such compounds.⁴

For these reasons, many efforts have been made to discover and synthesize new analogues of type **1** with different R substituents.⁵ In some cases such analogues have proven to be more effective than the natural mevinic acids.



Nevertheless, the synthesis of these compounds in optically pure form has turned out to be rather challenging, and it was always achieved in several steps either by means of asymmetric reactions or starting from optically active natural products.⁶

In principle (see Scheme I) the target lactone **1** could be directly prepared from the *syn*-1,3-diol ester **A**, which can be obtained by the diastereoselective reduction⁷ of

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