93% yield; chromatographed, TLC (SSF) R_f 0.28; IR 2960, 1655, 1365, 760, 625 cm^{-1}; ^{1}H NMR (300 MHz) δ 6.40 (m, 4 H), 2.80 (m, 4 H, allylic), 1.80 (m, 4 H); MS 132 (M^+), 131, 117, 115, 104, 91, 78, 65, 39.

6,6-Trimethylenefulvene[7a] (entry 3): 15 min reaction time; TLC (2% ether/SSF) R_f 0.5; 65% yield; IR 3090, 3060, 2980, 2950, 2900, 2795, 1675, 1465, 1402, 1360, 1230, 1093, 1063, 1020, 910, 863, 805, 758, 702 cm^{-1}; ^{1}H NMR (80 MHz) δ 6.5–6.2 (m, 4 H, vinyl), 3.11 (appar t, 4 H, J = 7.6), 2.13 (appar q, 2 H, J = 7.6).

6,6-(2-Methylpentamethylene)fulvene (entry 4): 7.5 h reaction time; 77% yield; 5 equiv of pyrrolidine; chromatographed, TLC (2% ether/SSF) R_f 0.50; IR 3100, 3065, 2930, 2860, 1630, 1462, 1370, 1350, 1082, 927, 902, 888, 860, 842, 800, 760, 678, 628 cm^{-1}. ^{1}H NMR (300 MHz) δ 6.61–6.48 (m, 4 H, 3.4–3.3) (m, 1 H, methine), 2.95–2.85 (appar d, 1 H, J = 14, allylic), 2.45 (appar t, 1 H, J = 4.8 , 13.5, allylic), 2.0–1.4 (m, 6 H, methylenes), 1.25 (d, 3 H, J = 7.2, methyl); MS 161 (M + 1)$^+$, 160 (M^+), 145, 131, 117, 115, 92, 91, 78, 39. Anal. Calcd, 160.1252; found, 160.1252.

4-Cyclopentadienylidenetetrahydrothiopyran (6)[17] (entry 5): 2 h 15 min reaction time; TLC (10% ether/SSF) R_f 0.50; chromatographed, 2% ether/SSF; 95% yield; IR 3102, 3072, 2968, 2910, 2850, 1725, 1726, 1640, 1467, 1430, 1420, 1380, 1368, 1322, 1290, 1232, 1148, 1130, 1110, 1094, 1024, 1003, 985, 950, 922, 895, 858, 828, 800, 768, 700, 680, 610 cm^{-1}; ^{1}H NMR (80 MHz) δ 6.57 (s, 4 H), 3.15–2.75 (m, 8 H); MS 165 (M + 1)$^+$, 164 (M^+), 135, 117, 116, 1158 103, 91, 90, 89, 78, 77, 65, 63, 62, 51, 50, 46, 45, 38 27. Anal. Calcd, 164.0660; found, 164.0653.

4-Cyclopentadienylidenetetrahydropyran (7)[17] (entry 6): 1.5 h reaction time; 86% yield; chromatographed (10% ether/SSF); TLC (30% ether/Skellysolve F) R_f 0.40; IR 3102, 3072, 2968, 2910, 2850, 1752, 1726, 1640, 1467, 1430, 1420, 1380, 1368, 1322, 1290, 1232, 1148, 1130, 1110, 1094, 1024, 1003, 685, 950, 922, 895, 858, 828, 800, 768, 700, 680, 610 cm^{-1}; ^{1}H NMR (80 MHz) δ 6.51 (s, 4 H), 3.83 (t, 4 H, J = 5.5, CH_2OCH_2), 2.74 (t, 4 H, allylic methylenes, J = 5.5); MS 149 (M + 1)$^+$, 148 (M^+), 117, 115, 103, 91, 90, 89, 78, 77, 39. Anal. Calcd, 148.0888; found, 148.0892.

6,6-Dimethylfulvene[8t] (entry 7): 12 min reaction time; TLC (SSF) R_f 0.34; chromatographed (SSF); 81% yield; ^{1}H NMR (300 MHz) δ 6.53–6.45 (m, 4 H), 2.19 (s, 6 H).

6-Cyclohexylfulvene (entry 8): 1 h reaction time; quantitative yield; TLC (SSF) R_f 0.40; IR 3100, 3070, 2920, 2850, 1648, 1475, 1447, 1380, 1334, 1068, 963, 898, 760, 610 cm^{-1}; ^{1}H NMR (300 MHz) δ 6.53–6.15 (m, 5 H), 2.9–2.7 (m, 1 H), 2.0–1.1 (m, 10 H); MS 160 (M^+), 117, 104, 92, 91, 79, 78, 39. Anal. Calcd, 160.1252; Found, 160.1251.

6-Isopropylfulvene[7b,8t] (entry 9): 15 min rection time using pyrrolidine and 2.5 h using diethylamine; 98% after 15 min (pyrrolidine) and 45% after 2.5 h (diethylamine); IR 3100, 3070, 2960, 2865, 1650, 1465, 1335, 1078, 890, 760, 610 cm^{-1}; ^{1}NMR (80 MHz) δ 6.53–6.10 (m, 5 H), 3.30–2.85 (m, 1 H), 1.12 (d, 6 H, J = 6.6); MS 120 (M^+), 105, 45, 31, 27.

6-*tert*-Butylfulvene[7b] (entry 10): 18 h reaction time; 90% yield; chromatographed (SSF); IR 3075, 2960, 2905, 2870, 1635, 1475, 1460, 1396, 1380, 1362, 1342, 1215, 1090, 1080, 880, 760, 618 cm^{-1}; ^{1}H NMR (300 MHz) δ 6.68–6.67 (m, 1 H), 6.60–6.57 (m, 1 H), 6.43 (br s, 1 H), 6.40–6.36 (m, 1 H), 6.17–6.14 (m, 1 H), 1.28 (s, 9 H); MS 134 (M^+), 119, 91, 77, 41, 39.

6-(1,1,4-Trimethyl-4-pentenyl)fulvene[3] (entry 11): 17 h reaction time; 59% yield; chromatographed; TLC (SSF) R_f 0.32; IR 3070, 1630, 885 cm^{-1}; ^{1}H NMR (300 MHz) δ 6.60–6.55 (m, 2 H), 6.40–6.30 (m, 2 H), 6.18–6.05 (7, 1 H), 4.70–4.60 (m, 2 H, $=CH_2$), 2.10–1.05 (m, 4 H, CH_2CH_2), 1.29 (s, 6 H, CMe_2). Anal. Calcd: C, 89.36; H, 10.63. Found: C, 89.15; H, 10.50.

6-Phenylfulvene[7b] (entry 12): 4.5 h reaction time using pyrrolidine and 23 h using diethylamine; TLC (pentane) R_f 0.38; chromatographed; 70% after 4.5 h (pyrrolidine) and 45% after 23 h (diethylamine). Detailed spectral data can be found in ref 7b and 21.

Optically pure fulvene 10 (entry 13): 48 h reaction time; 5 equiv pyrrolidine; 45% trans and 6% cis; chromatographed (5% ether/SSF); TLC (10% ether/Skellysolve F) R_f trans 0.55, cis 0.48; IR (cis) 3080, 2955, 2935, 2860, 1659, 1653, 1475, 1463, 1255, 1191, 1100, 995, 940, 896, 835, 778, 765, 615 cm^{-1}; ^{1}H NMR (300 MHz) δ 6.54–6.52 (m, 1 H), 6.48–6.45 (m, 2 H), 6.385 (apparent d, 1 H, C_6H, J = 9.0), 6.22–6.20 (m, 1 H), 5.526 (apparent d, 1 H, OCHO, J = 3.0), 5.04–4.95 (m, 1 H, allylic CH), 2.20–1.90 (m, 4 H), 0.904 (s, 9 H, *t*-Bu), 0.123 (s, 3 H, SiMe), 0.111 (s, 3 H, SiMe); MS 279, 263, 221, 201, 199, 171, 147, 145, 129, 119, 117, 103, 91, 75, 73. Anal. MS [CI, CH_5^+ source] calcd, 279.1780 (M + 1)$^+$; found, 279.1781. For the trans isomer: IR 3080, 2960, 2935, 2860, 1660, 1654, 1483, 1475, 1465, 1345, 1260, 1255, 1193, 1090, 1022, 995, 898, 840, 780, 765, 615 cm^{-1}; ^{1}H NMR (300 MHz) δ 6.55–6.47 (m, 2 H), 6.48–6.45 (m, 1 H), 6.281 (app d, 1 H, C_6H, J = 8.1 Hz), 6.191 (app dt, 1 H, J = 5.4, 1.5), 5.615 (app dd, 1 H, OCHO, J = 4.5, 1.5), 5.168 (app td, 1 H, allylic CH, J = 8.1, 6.3), 2.41–2.30 (m, 1 H), 2.15–2.05 (m, 1 H), 1.95–1.85 (m, 1 H, 1.80–1.68 (m, 1 H), 0.900 (s, 9 H, *t*-Bu), 0.119 (s, 6 H, $SiMe_2$); $[\alpha]_D^{25}$ (trans) +68.5 (*c* 1.55, $CHCl_3$). Anal. MS (CI) calcd, 279.1780 (M + 1)$^+$; found, 279.1808.

Registry No. 1 (E = CO_2CH_3), 89618-85-9; 2, 81331-92-2; 3, 87727-32-0; 4 (R = $SiMe_2Bu$-*t*), 87727-33-1; *cis*-4 (R = $SiMe_2Bu$-*t*), 89675-01-4; 6, 82235-10-7; 7, 82250-30-4; 6,6-pentamethylenefulvene, 3141-04-6; 6,6-tetramethylenefulvene, 4727-24-6; 6,6-trimethylenefulvene, 29183-43-5; 6,6-(2-methylpentamethylene)fulvene, 61039-47-2; 6,6-dimethylfulvene, 2175-91-9; 6-cyclohexylfulvene, 89618-84-8; 6-isopropylfulvene, 13912-68-0; 6-*tert*-butylfulvene, 24730-31-7; 6-phenylfulvene, 7338-50-3; 6-(2,2-dimethyl-4-pentenyl)fulvene, 89618-86-0; cyclopentadiene, 542-92-7; cyclohexanone, 108-94-1; cyclopentanone, 120-92-3; cyclobutanone, 1191-95-3; 2-methylcyclohexanone, 583-60-8; tetrahydrothiopyran-4-one, 1072-72-6; tetrahydropyran-4-one, 29943-42-8; acetone, 67-64-1; cyclohexanecarboxaldehyde, 2043-61-0; isobutyraldehyde, 78-84-2; pivalaldehyde, 630-19-3; 2,2,5-trimethyl-5-hexenal, 81331-91-1; benzaldehyde, 100-52-7; 3,3-dimethyl-6-(methoxycarbonyl)-5-hexenal, 89618-83-7; 3,3-dimethyl-5-hexenal, 39482-40-1; pyrrolidine, 123-75-1.

A Simple Conversion of 2-Methoxynaphthoquinones to 2,3,4,5-Tetrahydronaphtho[1,2-*b*]furan-4,5-diones. Application to the Synthesis of (±)-Trypethelones

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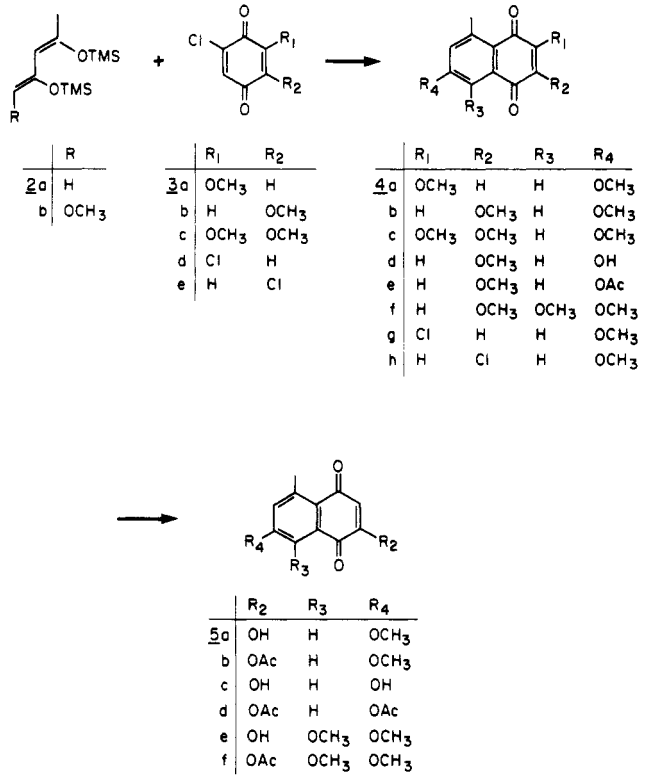
Structures proposed for trypethelone, *O*-methyltrypethelone, and *O*-methyl-8-methoxytrypethelone have been confirmed by synthesis. The required naphthoquinone substrates were prepared regiospecifically in one step by using vinylogous ketene acetals and then converted to the desired products essentially in a novel one-flask procedure.

Recently several naphthoquinones were isolated from the mycosymbiont of *Trypethelium eluteriae* Sprengel and identified on spectral grounds as substituted dunniones.[1] In principle the structures of these substances could be

0022-3263/84/1949-1853$01.50/0

Scheme I



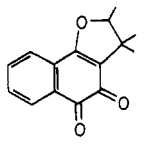
	R
2a	H
b	OCH_3

	R_1	R_2
3a	OCH_3	H
b	H	OCH_3
c	OCH_3	OCH_3
d	Cl	H
e	H	Cl

	R_1	R_2	R_3	R_4
4a	OCH_3	H	H	OCH_3
b	H	OCH_3	H	OCH_3
c	OCH_3	OCH_3	H	OCH_3
d	H	OCH_3	H	OH
e	H	OCH_3	H	OAc
f	H	OCH_3	OCH_3	OCH_3
g	Cl	H	H	OCH_3
h	H	Cl	H	OCH_3

	R_2	R_3	R_4
5a	OH	H	OCH_3
b	OAc	H	OCH_3
c	OH	H	OH
d	OAc	H	OAc
e	OH	OCH_3	OCH_3
f	OAc	OCH_3	OCH_3

confirmed by modifications of approaches developed for the synthesis of deoxyerythrolaccin[2] and erythrolaccin[3] combined with the classic procedure used for elaborating dunnione (1) itself.[4] (±)-Trypethelone (**8a**), (±)-*O*-



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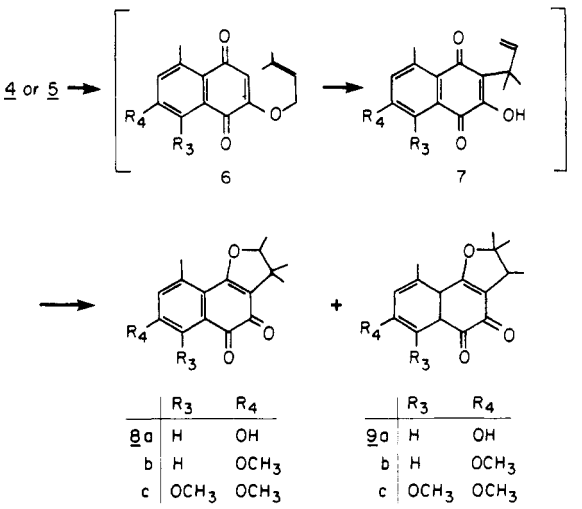
methyltrypethelone (**8b**), and (±)-*O*-methyl-8-methoxytrypethelone (**8c**) have now been obtained from readily prepared naphthoquinones by various modifications of this approach.

Convenient syntheses of the appropriately substituted naphthoquinones could be envisaged by the use of vinylogous ketene acetals and 2-chloro-5-methoxybenzoquinone (Scheme I). Several 2,4-dioxygenated pentadienes have been described, and it appears in particular that the 4-methoxy-2-trimethylsiloxy derivatives[2,5] are more satisfactory for the annulation of naphthoquinones while the 2-methoxy-4-trimethylsiloxy isomers[6] should be preferred for reactions with benzoquinones[7] (although spectral evidence is ambiguous, chemical behavior seems to indicate that enolsilylation of 4-methoxypent-3-en-2-one with triethylamine and chlorotrimethylsilane gives principally the 4-methoxy dienes while *N,O*-bis(trimethylsilyl)acetamide affords mainly the 2-methoxy isomers). These considerations and preliminary experiments suggested applying the

Scheme II



	R_3	R_4
8a	H	OH
b	H	OCH_3
c	OCH_3	OCH_3

	R_3	R_4
9a	H	OH
b	H	OCH_3
c	OCH_3	OCH_3

even more readily accessible 2,4-bis(trimethylsiloxy) derivatives[3,8] **2a,b** to the problem at hand.

Diene **2a** cycloadded efficiently to a number of benzoquinones **3a–e**, and the resultant crude adducts were converted directly to the naphthoquinones by pyrolysis and usually methylation in overall yields of 65–77%, thus improving substantially a previously obtained[2] conversion of 28% for **4g**. The quinones could also be isolated before etherification as is illustrated in the case of compound **4d**. Preparation of 3,5,6-trimethoxy-8-methylnaphthoquinone required for the synthesis of (±)-*O*-methyl-8-methoxytrypethelone (**8c**) was considerably more troublesome and seems to reflect the difficulty of bringing the 5-methoxy group into a hindered coplanar position. Various dienes such as 1,2,4-tris(trimethylsiloxy)-, 1,2-dimethoxy-4-(trimethylsiloxy)-, and 1,2-dimethoxy-1-(trimethylsiloxy)-pentadienes either could not be obtained satisfactorily or else gave very poor results. Eventually, 1-methoxy-2,4-bis(trimethylsiloxy)pentadiene (**2b**) was induced under precise conditions to provide a 37% yield of the elusive naphthoquinone **4f**.

Originally dimethoxynaphthoquinone **4b** was converted to the monohydroxy compound **5a** by basic hydrolysis[9] in nearly quantitative yield. Efficient O-alkylation with isoprenyl bromide could be carried out by application of HSAB principles,[10,11] i.e., by the use of silver(I) oxide in a dipolar aprotic solvent (HMPT). The resultant allyl ether **6** was found to be much more sensitive than the parent substance described by Cooke[4] and could not be recrystallized without partial rearrangement. However the crude material did not contain an isolable amount of the C-alkylated product and was transposed directly by refluxing in ethanol for 20 h. After evaporation, treatment of the residue with cold concentrated sulfuric acid for 5 min gave the expected *O*-methyltrypethelone **8b** in an overall yield of 36%. Rearrangement was not accompanied by a detectable quantity of the "abnormal" product, but cyclization, in spite of milder conditions, invariably produced some of the corresponding β-isotrypethelone **9b** (7%) (the latter is named by analogy with dunnione chemistry) (Scheme II).

Subsequently it was found advantageous to isolate the hydrolyzed compound **5a** as the acetate **5b** and observed

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(6) Cameron, D. W.; Deutscher, D. J.; Feutrill, G. I.; Griffiths, P. G. *Aust. J. Chem.* **1981**, *34*, 2401.
(7) Roberge, G.; Brassard, P. unpublished results.
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(11) Huot, R.; Brassard, P. *Can. J. Chem.* **1974**, *52*, 88.

that it could be transformed directly into the allyl ether **6** under similar conditions (method D) and in comparable yield as with the hydroxyquinone. Eventually the same treatment was applied successfully to the original methyl ether **4b** (method E) allowing this part of the process to be conducted as a one-flask procedure and the whole synthesis essentially in two steps. Reactive substrates such as **4b** and **5b** (the vinylogues of esters or anhydrides) are probably converted by the basic oxide to the corresponding silver salt and alkylated in the usual way.

The preparation of (±)-trypethelone itself (**8a**) was considered from a slightly different approach. The cycloaddition product obtained from **2a** and **3b** was aromatized; the resulting naphthoquinone **4d** was hydrolyzed under acidic conditions[12] and converted to the diacetate **5d** (the dihydroxy compound **5c** was also isolated and, on the basis of its spectral characteristics, was obviously identical with the natural product described previously[13,14]). Application of method D to this substrate gave (±)-trypethelone (**8a**) smoothly in 32% along with the expected byproduct β-isotrypethelone **9a** (9%). The simplified procedure (method E) starting with the methoxyquinone **4e** afforded a slightly better yield (39%) of the natural product and less of the rearranged compound (4%). In both cases only the more reactive functions, i.e., on the quinonic ring (being vinylogous esters or anhydrides), are affected.

Synthesis of (±)-*O*-methyl-8-methoxytrypethelone (**8c**) was carried out substantially as for **8b** by O-allylation of hydroxyquinone **5e** and provided the tricyclic quinone **8c** in 35% yield (with 10% of the β-iso compound **9c**). Similar results were obtained from the acetate **5f** (method D) while application of method E directly to methoxyquinone **4f** proved to be unexpectedly difficult resulting in a mere 7% conversion to **8c**.

All of the natural trypethelones were isolated in very small amounts and seem to be unavailable for comparison with the racemic materials. However extensive spectral data have been published and are in good agreement with those of the synthetic substances.

Note Added in Proof: Comparison (IR and TLC) of the synthetic materials with optically active **8a** and **8c** as well as with racemic **8b**, kindly provided by Professor W. Steglich, showed excellent concordance.

Experimental Section

All melting points were taken for samples in capillary tubes with a Thomas-Hoover Apparatus and are not corrected. The UV spectra were determined on a Hewlett-Packard 8450A spectrophotometer and the IR spectra on a Beckman Model IR-4250 instrument calibrated with a film of polystyrene. NMR spectra were recorded with a Bruker HX-90 spectrometer using tetramethylsilane as internal standard. Mass spectra were obtained with a Hewlett-Packard 5995A spectrometer. Woelm silica gel, activity III, and Merck silica gel $60F_{254}$, both for dry column chromatography, were used throughout in a product to adsorbent ratio of 1:50–100. Elemental analyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn. Exact masses were provided by the Laboratoire de Spectrométrie de Masse, Université de Sherbrooke, Sherbrooke, Quebec.

Preparation of 2- and 3-Methoxy- or 2- and 3-Chloronaphthoquinones 4a–h. Method A. A solution of the benzoquinone (2.00 mmol) and diene **2a** (2.50 mmol) in dry THF (10–15 mL) was refluxed for 2–20 h and evaporated to dryness. After pyrolysis in an open flask at 120 °C for 1–2 h and methylation [CH_3I (6 mmol), Ag_2O (4 mmol), and $CHCl_3$ (50 mL) at 25 °C (15 h)], the expected product was isolated by chromatography (benzene–ethyl acetate, 5–10:1).

Method B. To the benzoquinone (2.00 mmol) in THF (10 mL) was added, over 30 min at −25 °C, 2.30 mmol of the diene in the same solvent (10 mL). The solution was allowed to reach room temperature slowly, then refluxed for 1 h, and evaporated and the residue pyrolyzed and methylated as in method A. Isolation of the naphthoquinone was carried out by chromatography (benzene).

2,6-Dimethoxy-8-methylnaphthoquinone (4a). Naphthoquinone **4a** (359 mg, 77%) was obtained from benzoquinone **3a**[15] and diene **2a** (method A, 2 h): mp 183.5 °C (benzene–petroleum ether, bp 65–110 °C); IR ν_{max} (KBr) 1668, 1645, 1615, 1590, 1558 cm^{-1}; UV λ_{max} (MeOH) 266, 290, 337, 400 nm (log ε 4.25, 4.17, 3.50, 3.12); NMR ($CDCl_3$) δ 2.71 (3 H, s, 8-CH_3), 3.92, 3.96 (2 × 3 H, 2s, 2,6-OCH_3), 6.11 (1 H, s, 3-H), 6.94 (1 H, d, J = 3.0 Hz, 7-H), 7.48 (1 H, d, J = 3.0 Hz, 5-H); mass spectrum, m/e 232 (M^+). Anal. Calcd for $C_{13}H_{12}O_4$: C, 67.23; H, 5.21. Found: C, 67.28; H, 5.27.

3,6-Dimethoxy-8-methylnaphthoquinone (4b). A reaction between benzoquinone **3b**[15] and diene **2a** (method A, 12 h) gave naphthoquinone **4b** (336 mg, 72%): mp 169.0–169.5 °C (chloroform–petroleum ether, bp 65–110 °C) (lit.[13] mp 172.0–173.5 °C lit.[14] mp 172–173 °C); IR ν_{max} ($CHCl_3$) 1680, 1645, 1628, 1595, 1560 cm^{-1}; UV λ_{max} (EtOH) 263, 291, 343, 400 nm (log ε 4.36, 4.13, 3.42, 3.25); NMR ($CDCl_3$) δ 2.74 (3 H, s, 8-CH_3), 3.89, 3.95 (2 × 3 H, 2s, 3,6-OCH_3), 6.08 (1 H, s, 2-H), 7.02 (1 H, d, J = 3.0 Hz, 7-H), 7.57 (1 H, d, J = 3.0 Hz, 5-H); mass spectrum, m/e 232 (M^+).

2,3,6-Trimethoxy-8-methylnaphthoquinone (4c). An analogous reaction using quinone **3c**[16] and diene **2a** (method A, 20 h) afforded naphthoquinone **4c** (340 mg, 65%): mp 107.5 °C (benzene–petroleum ether, bp 65–110 °C); IR ν_{max} (KBr) 1665, 1625, 1600, 1560 cm^{-1}; UV λ_{max} (MeOH) 266, 298, 344, 400 nm (log ε 4.39, 4.12, 3.62, 3.11); NMR ($CDCl_3$) δ 2.63 (3 H, s, 8-CH_3), 3.92, 4.08, 4.14 (3 × 3 H, 3s, 2,3,6-OCH_3), 6.84 (1 H, d, J = 2.5 Hz, 7-H), 7.35 (1 H, d, J = 2.5 Hz, 5-H); mass spectrum, m/e 262 (M^+). Anal. Calcd for $C_{14}H_{14}O_5$: C, 64.12; H, 5.38. Found: C, 64.41; H, 5.43.

6-Hydroxy-3-methoxy-8-methylnaphthoquinone (4d). A benzene solution (50 mL) of benzoquinone **3b** (10.0 mmol) and diene **2a** (11.0 mmol) was refluxed for 24 h. After pyrolysis of the residue, the crude product was dissolved in ethyl acetate (750 mL) and extracted with 5% Na_2CO_3 (2 × 400 mL). The aqueous solution was then washed with ether (500 mL), acidified, and extracted with ethyl acetate (3 × 500 mL), giving the hydroxyquinone **4d** (1.222 g, 56%): mp 261 °C dec (ethyl acetate–petroleum ether, bp 65–110 °C); IR ν_{max} (KBr) 3300, 1680, 1625, 1600, 1555 cm^{-1}; UV λ_{max} (MeOH) 264, 291, 344, 402 nm (log ε 4.35, 4.12, 3.36, 3.25); NMR [$(CD_3)_2SO$] δ 2.61 (3 H, s, 8-CH_3), 3.83 (3 H, s, 3-OCH_3), 6.16 (1 H, s, 2-H), 6.99 (1 H, d, J = 3.0 Hz, 7-H), 7.31 (1 H, d, J = 3.0 Hz, 5-H); mass spectrum, m/e 218 (M^+). Anal. Calcd for $C_{12}H_{10}O_4$: C, 66.05; H, 4.62. Found: C, 66.25; H, 4.56.

6-Acetoxy-3-methoxy-8-methylnaphthoquinone (4e). Acetylation (Ac_2O–H_2SO_4) of quinone **4d** gave the acetoxynaphthoquinone **4e** (92%): mp 185 °C (benzene–petroleum ether, bp 65–110 °C); IR ν_{max} (KBr) 1765, 1680, 1650, 1625, 1595, 1575 cm^{-1}; UV λ_{max} (MeOH) 250, 281, 341 nm (log ε 4.23, 4.09, 3.45); NMR ($CDCl_3$) δ 2.34 (3 H, s, 6-OAc), 2.76 (3 H, s, 8-CH_3), 3.90 (3 H, s, 3-OCH_3), 6.14 (1 H, s, 2-H), 7.29 (1 H, d, J = 2.5 Hz, 7-H), 7.81 (1 H, d, J = 2.5 Hz, 5-H); mass spectrum, m/e 260 (M^+). Anal. Calcd for $C_{14}H_{12}O_5$: C, 64.61; H, 4.65. Found: C, 64.64; H, 4.78.

3,5,6-Trimethoxy-8-methylnaphthoquinone (4f). A solution of benzoquinone **3b** (2.00 mmol) and diene **2b** (2.50 mmol) in dry benzene (15 mL) was refluxed for 20 h, diluted with a 2:1 mixture (10 mL) of methanol and 5% aqueous HCl, boiled for 1 h, poured into water, and extracted with ether. The residue was methylated in a standard way [$(CH_3)_2SO_4$ (8.0 mmol), K_2CO_3 (8.8 mmol), and $(CH_3)_2CO$ (125 mL) (2.5 h)] and after chromatography (benzene–ethyl acetate, 3:1) yielded the desired quinone **4f** (196 mg,

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37%): mp 185.0–186.5 °C (benzene–petroleum ether, bp 65–110 °C); IR ν_{max} (KBr) 1675, 1630, 1623, 1585, 1545 cm^{-1}; UV λ_{max} (MeOH) 263, 287, 396 nm (log ϵ 4.32, 4.05, 3.56); NMR ($CDCl_3$) δ 2.70 (3 H, s, 8-CH_3), 3.88, 3.92, 3.98 (3 × 3 H, 3s, 3,5,6-OCH_3), 6.03 (1 H, s, 2-H), 7.01 (1 H, s, 7-H); mass spectrum, m/e 262 (M^+). Anal. Calcd for $C_{14}H_{14}O_5$: C, 64.12; H, 5.38. Found: 64.40; H, 5.44.

2-Chloro-6-methoxy-8-methylnaphthoquinone (4g). Condensation of benzoquinone **3d**[17] and diene **2a** (method B) provided naphthoquinone **4g** (332 mg, 70%), mp 162.5 °C (benzene–petroleum ether, bp 65–110 °C) (lit.[2] mp 161–162 °C), indistinguishable from a previously prepared sample: IR ν_{max} (KBr) 1680, 1665, 1590 cm^{-1}.

3-Chloro-6-methoxy-8-methylnaphthoquinone (4h). A similar reaction with benzoquinone **3e**[17] and diene **2a** (method B) gave naphthoquinone **4h** (338 mg, 71%): mp 158.5–159.0 °C (benzene–petroleum ether, bp 65–110 °C); IR ν_{max} (KBr) 1680, 1650, 1610, 1590, 1550 cm^{-1}; UV λ_{max} (MeOH) 254, 275 (sh), 330 nm (log ϵ 4.20, 3.92, 3.48); NMR ($CDCl_3$) δ 2.72 (3 H, s, 8-CH_3), 3.97 (3 H, s, 6-OCH_3), 7.03 (1 H, d, J = 3.0 Hz, 7-H), 7.09 (1 H, s, 2-H), 7.56 (1 H, d, J = 3.0 Hz, 5-H); mass spectrum, m/e 236/238 (M^+). Anal. Calcd for $C_{12}H_9ClO_3$: C, 60.90; H, 3.83; Cl, 14.98. Found: C, 61.14; H, 3.80; Cl, 15.05.

3-Hydroxy- and 3-Acetoxy-8-methylnaphthoquinones. The 3-hydroxyquinones were obtained from the ethers either by saponification[9] in 1.5% aqueous NaOH or by acid hydrolysis[12] in a 1:1 mixture of acetic and concentrated hydrochloric acids and are sufficiently pure to be acetylated directly.

3-Hydroxy-6-methoxy-8-methylnaphthoquinone (5a). Naphthoquinone **5a** (99%) was obtained from ether **4b** (20.0 mmol) by basic hydrolysis (100 °C, 1 h): mp 176 °C (ethyl acetate–petroleum ether, bp 65–110 °C) (lit.[13] mp 180.0–182.5 °C); IR ν_{max} (KBr) 3000 (br), 1680, 1615, 1590, 1545 cm^{-1}; UV λ_{max} (EtOH containing 1% HCO_2H) 262, 295, 344, 408 nm (log ϵ 4.33, 4.09, 3.50, 3.10); NMR [$(CD_3)_2SO$] δ 2.64 (3 H, s, 8-CH_3), 3.91 (3 H, s, 6-OCH_3), 6.06 (1 H, s, 2-H), 7.19 (1 H, d, J = 3.0 Hz, 7-H), 7.39 (1 H, d, J = 3.0 Hz, 5-H).

3-Acetoxy-6-methoxy-8-methylnaphthoquinone (5b). Acetylation (Ac_2O–H_2SO_4) of the preceding hydroxy compound **5a** gave the corresponding acetate **5b** (88%): mp 100–101 °C dec (benzene–petroleum ether, bp 65–110 °C); IR ν_{max} (KBr) 1775, 1675, 1660, 1640, 1595, 1560 cm^{-1}; UV λ_{max} (MeOH) 243, 264 (sh), 299 (sh), 333 (sh) nm (log ϵ 4.23, 4.04, 3.73, 3.55); NMR ($CDCl_3$) δ 2.39 (3 H, s, 3-OAc), 2.73 (3 H, s, 8-CH_3), 3.94 (3 H, s, 6-OCH_3), 6.66 (1 H, s, 2-H), 7.04 (1 H, d, J = 3.0 Hz, 7-H), 7.54 (1 H, d, J = 3.0 Hz, 5-H); mass spectrum, m/e 260 (M^+). Anal. Calcd for $C_{14}H_{12}O_5$: C, 64.61; H, 4.65. Found: C, 64.49; H, 4.77.

3,6-Dihydroxy-8-methylnaphthoquinone (5c). Acid hydrolysis (90 °C, 30 min) of ether **4d** (1.00 mmol) gave naphthoquinone **5c** (95%): mp >255 °C dec (methanol–chloroform) (lit.[13] mp >260 °C dec, lit.[14] >250 °C dec); IR ν_{max} (KBr) 3330 (br), 1670, 1660, 1625, 1605, 1550 cm^{-1}; UV λ_{max} (EtOH) 265, 296, 348 nm (log ϵ 4.31, 4.05, 3.46); NMR [$(CD_3)_2SO$] δ 2.61 (3 H, s, 8-CH_3), 6.04 (1 H, s, 2-H), 6.97 (1 H, d, J = 2.5 Hz, 7-H), 7.33 (1 H, d, J = 2.5 Hz, 5-H). Anal. Calcd for $C_{11}H_8O_4$: C, 64.71; H, 3.95. Found: C, 64.92; H, 4.03.

3,6-Diacetoxy-8-methylnaphthoquinone (5d). Acetylation (Ac_2O–H_2SO_4) of the dihydroxy compound **5c** afforded naphthoquinone **5d** (88%): mp 104–105 °C (benzene–petroleum ether, bp 65–110 °C); IR ν_{max} (KBr) 1780, 1765, 1680, 1663, 1642, 1598 cm^{-1}; UV λ_{max} (MeOH) 238, 290 (sh), 340 (sh) nm (log ϵ 4.25, 3.66, 3.45); NMR ($CDCl_3$) δ 2.36, 2.39 (2 × 3 H, 2s, 3,6-OAc), 2.77 (3 H, s, 8-CH_3), 6.73 (1 H, s, 2-H), 7.33 (1 H, d, J = 2.5 Hz, 7-H), 7.79 (1 H, d, J = 2.5 Hz, 5-H); mass spectrum, m/e 288 (M^+). Anal. Calcd for $C_{15}H_{12}O_6$: C, 62.50; H, 4.20. Found: C, 62.70; H, 4.17.

3-Hydroxy-5,6-dimethoxy-8-methylnaphthoquinone (5e). Ether **4f** (1.00 mmol) was converted by acid hydrolysis (90 °C, 15 min) to the corresponding hydroxyquinone **5e** in 98% yield: mp 216.0–216.5 °C (1,2-dichloroethane–petroleum ether, bp 65–110 °C); IR ν_{max} (KBr) 3345, 1657, 1635, 1580, 1540 cm^{-1}; UV λ_{max} (MeOH) 263, 290, 361, 408 nm (log ϵ 4.30, 4.01, 3.52, 3.42); NMR [$(CD_3)_2SO$] δ 2.62 (3 H, s, 8-CH_3), 3.80 (3 H, s, 6-OCH_3), 3.96 (3 H, s, 5-OCH_3), 6.01 (1 H, s, 2-H), 7.27 (1 H, s, 7-H); mass spectrum, m/e 248 (M^+). Anal. Calcd for $C_{13}H_{12}O_5$: C, 62.90; H, 4.87. Found: C, 62.90; H, 4.99.

3-Acetoxy-5,6-dimethoxy-8-methylnaphthoquinone (5f). Hydroxyquinone **5e** was converted in the usual way to the corresponding acetate **5f** (82%): mp 171.5–172.5 °C (benzene–petroleum ether, bp 65–110 °C); IR ν_{max} (KBr) 1765, 1670, 1660, 1640, 1580, 1545 cm^{-1}; UV λ_{max} (MeOH) 243, 322 nm (log ϵ 4.22, 3.68); NMR ($CDCl_3$) δ 2.39 (3 H, s, 3-OAc), 2.73 (3 H, s, 8-CH_3), 3.92 (3 H, s, 6-OCH_3), 4.00 (3 H, s, 5-OCH_3), 6.61 (1 H, s, 2-H), 7.02 (1 H, s, 7-H); mass spectrum, m/e 290 (M^+). Anal. Calcd for $C_{15}H_{14}O_6$: C, 62.07; H, 4.86. Found: C, 62.04; H, 4.84.

Synthesis of Trypethelones. Method C. In a typical experiment, a suspension of the 3-hydroxynaphthoquinone (4.60 mmol), freshly distilled isoprenyl bromide (10.0 mmol), silver(I) oxide (10.0 mmol), and dry HMPT (25 mL) was stirred for 18 h at room temperature, then diluted with ether, washed repeatedly with water, dried, and evaporated. The residue was taken up in absolute ethanol (100 mL), refluxed for 24 h, and again evaporated. Cold concentrated H_2SO_4 (15 mL) was then added and the mixture stirred at 0 °C for 5 min and poured into ice water. The products were extracted with ethyl acetate and separated by chromatography (benzene–ethyl acetate, 5:1).

Method D. A mixture of the 3-acetoxynaphthoquinone (1.07 mmol), isoprenyl bromide (4.00 mmol), and silver(I) oxide (3.50 mmol) in dry HMPT (8 mL) was stirred at room temperature for 24 h, diluted with ether, washed several times with water, dried, and evaporated. The residue was refluxed in absolute ethanol (25 mL) for 20 h, evaporated, dissolved in cold concentrated H_2SO_4 (5 mL), stirred for 5 min at 0 °C, and poured into ice water. Isolation and purification of products were carried out as in method C.

Method E. A representative example consisted of stirring a suspension of the 3-methoxynaphthoquinone (1.00 mmol), silver(I) oxide (8.00 mmol), and isoprenyl bromide (10.0 mmol) in dry HMPT (8 mL) for 24 h. The rest of the procedure was conducted as in method D.

(±)-2,3,4,5-Tetrahydro-7-methoxy-2,3,3,9-tetramethylnaphtho[1,2-*b*]furan-4,5-dione [(±)-Trypethelone Methyl Ether] (8b). (a) Method C using quinone **5a** (1.01 g, 4.60 mmol) afforded 477 mg (36%) of the ether **8b**: mp 185.0–185.5 °C (toluene–petroleum ether, bp 90–120 °C) (lit.[1] mp (+) isomer 140–142 °C); IR ν_{max} (KBr) 1645, 1635, 1605, 1585, 1552, 1452, 1390, 1380, 1338, 1295, 1285, 1255, 1165, 1132, 1105, 1055, 1018, 970, 880, 788 cm^{-1}; UV λ_{max} (MeOH) 273, 283, 314, 500 nm (log ϵ 4.43, 4.45, 3.76, 3.35); NMR [$(CD_3)_2CO$] δ 1.22, 1.40 (2 × 3 H, 2s, 3,3-CH_3), 1.47 (3 H, d, J = 7.0 Hz, 2-CH_3), 2.60 (3 H, s, 9-CH_3), 3.90 (3 H, s, 7-OCH_3), 4.67 (1 H, q, J = 7.0 Hz, 2-H), 7.03 (1 H, d, J = 3.0 Hz, 8-H), 7.34 (1 H, d, J = 3.0 Hz, 6-H); mass spectrum, m/e 286 (M^+). Anal. Calcd for $C_{17}H_{18}O_4$: C, 71.31; H, 6.34. Found: C, 71.42; H, 6.42.

A second band consisted of (±)-2,3,4,5-tetrahydro-7-methoxy-2,2,3,9-tetramethylnaphtho[1,2-*b*]furan-4,5-dione [(±)-β-isotrypethelone methyl ether] (**9b**) (94 mg, 7%): mp 180.5–181.5 °C (toluene–petroleum ether, bp 90–120 °C); IR ν_{max} (KBr) 1695, 1640, 1630, 1605, 1580, 1550 cm^{-1}; UV λ_{max} (MeOH) 278, 313, 504 nm (log ϵ 4.43, 3.81, 3.30); NMR ($CDCl_3$) δ 1.23 (3 H, d, J = 7.0 Hz, 3-CH_3), 1.52, 1.56 (2 × 3 H, 2s, 2,2-CH_3), 2.59 (3 H, s, 9-CH_3), 3.06 (1 H, q, J = 7.0 Hz, 3-H), 3.89 (3 H, s, 7-OCH_3), 7.01 (1 H, d, J = 3.0 Hz, 8-H), 7.33 (1 H, d, J = 3.0 Hz, 6-H); mass spectrum, m/e 286 (M^+). Anal. Calcd for $C_{17}H_{18}O_4$: C, 71.31; H, 6.34. Found: C, 71.48; H, 6.49.

(b) According to method D, acetate **5b** (278 mg, 1.07 mmol) provided 42% of **8b** and 8% of **9b**.

(c) Method E using ether **4b** (232 mg, 1.00 mmol) gave 27% of **8b** and 3% of **9b**.

(±)-2,3,4,5-Tetrahydro-7-hydroxy-2,3,3,9-tetramethylnaphtho[1,2-*b*]furan-4,5-dione [(±)-Trypethelone] (8a). (a) Method D applied to the diacetate **5d** (640 mg, 2.20 mmol) gave (±)-trypethelone (**8a**) (200 mg, 32%): mp 259.5–260.0 °C (1,2-dichloroethane–petroleum ether, bp 65–110 °C) (lit.[1] mp (+) isomer 264–266 °C); IR ν_{max} (KBr) 3080 (br), 1690, 1610, 1530, 1450, 1380, 1310, 1295, 1230, 1215, 1175, 1135, 1110, 1030, 870, 800, 690 cm^{-1}; UV λ_{max} (MeOH) 275, 284, 314, 522 nm (log ϵ 4.47, 4.49, 3.80, 3.38); NMR [$(CD_3)_2CO$] δ 1.24, 1.42 (2 × 3 H, 2s, 3,3-CH_3), 1.48 (3 H, d, J = 7.0 Hz, 2-CH_3), 2.59 (3 H, s, 9-CH_3), 4.74 (1 H, q, J = 7.0 Hz, 2-H), 6.99 (1 H, d, J = 3.0 Hz, 8-H), 7.39

(17) Available from Eastman Kodak Co.

(1 H, d, J = 3.0 Hz, 6-H); mass spectrum, m/e 272 (M^+). Anal. Calcd for $C_{16}H_{16}O_4$: C, 70.58; H, 5.92. Found: C, 70.38; H, 5.96.

A slower moving zone yielded (±)-2,3,4,5-tetrahydro-7-hydroxy-2,2,3,9-tetramethylnaphtho[1,2-*b*]furan-4,5-dione [(±)-β-isotrypethelone] (**9a**) (52 mg, 9%), mp 213-214 °C dec (1,2-dichloroethane-petroleum ether, bp 65-110 °C); IR ν_{max} (KBr) 3460 (br), 1690, 1605, 1585, 1525 cm^{-1}; UV λ_{max} (MeOH) 275, 280, 314, 516 nm (log ϵ 4.36, 4.37, 3.76, 3.24); NMR [$(CD_3)_2SO$] δ 1.17 (3 H, d, J = 7.0 Hz, 3-CH_3), 1.43 (6 H, s, 2,2-CH_3), 2.53 (3 H, s, 9-CH_3), 3.03 (1 H, q, J = 7.0 Hz, 3-H), 6.89 (1 H, d, J = 3.0 Hz, 8-H), 7.25 (1 H, d, J = 3.0 Hz, 6-H); $C_{16}H_{16}O_4$ requires 272.1048, found 272.1052.

(b) Method E using ether **4e** (260 mg, 1.00 mmol) gave 105 mg (39%) of **8a** and 10 mg (4%) of **9a**.

(±)-2,3,4,5-Tetrahydro-6,7-dimethoxy-2,3,3,9-tetramethylnaphtho[1,2-*b*]furan-4,5-dione [(±)-8-Methoxytrypethelone Methyl Ether] (8c). (a) Application of method C to hydroxyquinone **5e** (220 mg, 0.889 mmol) afforded (±)-8-methoxytrypethelone methyl ether (**8c**) (98 mg, 35%): mp 173.0-173.5 °C (toluene-petroleum ether, bp 90-120 °C) (lit.[1] mp (+) isomer 165-166 °C); IR ν_{max} (KBr) 1695, 1638, 1602, 1565, 1485, 1440, 1415, 1345, 1260, 1100, 1060, 1035, 1005, 985, 930, 875, 780 cm^{-1}; UV λ_{max} (MeOH) 276, 310 (sh), 369, 474 nm (log ϵ 4.45, 3.72, 3.42, 3.56); NMR [$(CD_3)_2CO$] δ 1.23, 1.40 (2 × 3 H, 2s, 3,3-CH_3), 1.48 (3 H, d, J = 7.0 Hz, 2-CH_3), 2.62 (3 H, s, 9-CH_3), 3.83 (3 H, s, 7-OCH_3), 3.98 (3 H, s, 6-OCH_3), 4.71 (1 H, q, J = 7.0 Hz, 2-H), 7.17 (1 H, s, 8-H); mass spectrum, m/e 316 (M^+). Anal. Calcd for $C_{18}H_{20}O_5$: C, 68.34; H, 6.37. Found: C, 68.33; H, 6.50.

Continued elution isolated (±)-2,3,4,5-tetrahydro-6,7-dimethoxy-2,2,3,9-tetramethylnaphtho[1,2-*b*]furan-4,5-dione [(±)-8-methoxy-β-isotrypethelone methyl ether] (**9c**) (29 mg, 10%): mp 161-163 °C (benzene-petroleum ether, bp 65-110 °C); IR ν_{max} (KBr) 1690, 1635, 1600, 1560 cm^{-1}; UV λ_{max} (MeOH) 276, 310 (sh), 369, 470 nm (log ϵ 4.37, 3.69, 3.35, 3.43); NMR ($CDCl_3$) δ 1.24 (3 H, d, J = 7.0 Hz, 3-CH_3), 1.48 (6 H, s, 2,2-CH_3), 2.63 (3 H, s, 9-CH_3), 3.14 (1 H, q, J = 7.0 Hz, 3-H), 3.91, 3.93 (2 × 3 H, 2s, 6,7-OCH_3), 6.87 (1 H, s, 8-H); $C_{18}H_{20}O_5$ requires 316.1311, found 316.1309.

(b) Method D using acetate **5f** (213 mg, 0.730 mmol) gave 84 mg (36%) of **8c** and 22 mg (9%) of **9c**.

(c) According to method E, ether **4f** (262 mg, 1.00 mmol) provided 23 mg (7%) of **8c** and 7 mg (2%) of **9c**.

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Registry No. **2a**, 68225-97-8; **2b**, 76665-75-3; **3a**, 54490-80-1; **3b**, 24605-23-0; **3c**, 30839-34-0; **3d**, 697-91-6; **3e**, 615-93-0; **4a**, 89827-85-0; **4b**, 41634-17-7; **4c**, 89827-86-1; **4d**, 89827-87-2; **4e**, 89827-88-3; **4f**, 89827-89-4; **4g**, 69122-32-3; **4h**, 89827-90-7; **5a**, 78239-27-7; **5b**, 89827-91-8; **5c**, 41634-16-6; **5d**, 89827-92-9; **5e**, 89827-93-0; **5f**, 89827-94-1; (±)-**8a**, 89887-33-2; (±)-**8b**, 89887-34-3; (±)-**8c**, 89887-35-4; (±)-**9a**, 89827-95-2; (±)-**9b**, 89827-96-3; (±)-**9c**, 89827-97-4; isoprenyl bromide, 870-63-3.

Reactions of 1,2-Naphthoquinones with Allyltrialkyltins

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BF_3-mediated allylation of 1,2-naphthoquinone and its 3-substituted derivatives with allyl-, (2-methyl-2-propenyl)-, *trans*-2-butenyl-, and (3-methyl-2-butenyl)trialkyltin afforded selectively the corresponding 4-allyl-1,2-naphthalenediols, which were isolated as diacetate or quinone. In the reactions with *trans*-2-butenyltributyltin, the regioisomer ratio of the α- vs. γ-adduct depends on the nature of substituents in position 3 of quinones. The reactions with (3-methyl-2-butenyl)tributyltin afforded α-adducts exclusively. Whether the reactions proceed toward 1,2-addition or 1,4-addition depends both on the electronic characteristics of the substituents and on the bulkiness of allyl moieties.

It is well-known that isoprenoid quinones play an important role in biological processes such as electron transport, blood clotting, and oxidative phosphorylation. The usual method of synthesis of these compounds involved a Lewis acid-catalyzed reaction between the appropriate allylic alcohol and hydroquinone, followed by mild oxidation to the quinone.[1] This method suffers from several side reactions such as cyclization of the unsaturated side chain, formation of the chromanol derivative, and polyalkylation of the aromatic ring. Despite a number of modifications, e.g., the use of allylic halides and masked quinones, the reaction remains limited because of the inherent instability of allylic components under the conditions employed.[2] Although the direct reaction of π-allylnickel bromide complexes with quinones[3] has been developed in the past decade, this method also remains fundamentally limited in the aspects of the yields, the regio- and stereoselectivity, and the availability of the starting materials. Recently, we published on the direct introduction of an allyl or a prenyl group into *p*-quinones using allyltin reagents in the presence of BF_3·OEt_2. The method has overcome all of the limitations described above.[4] Employing this method K. Maruyama and his co-workers prepared naturally occurring isoprenylquinones such as members of coenzyme Q series,[5,6] vitamin K series,[6,7] plastoquinone-1,[5] and plastoquinone-2[6] in satisfactory yields. Application of this allylating method to 1,2-naphthoquinones will open an additional new area for synthesizing a variety of physiologically active quinonoids.

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