(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 $\nu_{max}$ (KBr) 3460 (br), 1690, 1605, 1585, 1525 cm$^{-1}$; UV $\lambda_{max}$ (MeOH) 275, 280, 314, 516 nm (log $\epsilon$ 4.36, 4.37, 3.76, 3.24); NMR [$(CD_3)_2SO$] $\delta$ 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 $\nu_{max}$ (KBr) 1695, 1638, 1602, 1565, 1485, 1440, 1415, 1345, 1260, 1100, 1060, 1035, 1005, 985, 930, 875, 780 cm$^{-1}$; UV $\lambda_{max}$ (MeOH) 276, 310 (sh), 369, 474 nm (log $\epsilon$ 4.45, 3.72, 3.42, 3.56); NMR [$(CD_3)_2CO$] $\delta$ 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 $\nu_{max}$ (KBr) 1690, 1635, 1600, 1560 cm$^{-1}$; UV $\lambda_{max}$ (MeOH) 276, 310 (sh), 369, 470 nm (log $\epsilon$ 4.37, 3.69, 3.35, 3.43); NMR ($CDCl_3$) $\delta$ 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**.

**Acknowledgment.** We gratefully acknowledge financial support and bursaries (V.G.) from the Natural Sciences and Engineering Research Council of Canada and the Fonds F.C.A.C. (Gouvernement du Québec).

**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

Akio Takuwa,* Yoshinori Naruta,† Osamu Soga, and Kazuhiro Maruyama*†

*Department of Chemistry, Faculty of Science, Shimane University, Matsue 690, Japan, and Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606, Japan*

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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.

†Kyoto University.

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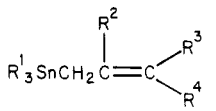
Table I. 3-Substituted 1,2-Naphthoquinones and Their Chemical Shifts of Proton $H_4$ Attached to the $C_4$-Carbon

| quinones | substituents | chemical shift of $H_4$, δ ($CDCl_3$) |
|---|---|---|
| 1,2-naphthoquinone (1a) | H | 7.44[a] |
| 3-nitro-1,2-naphthoquinone (1b) | $NO_2$ | 8.32 |
| 3-acetyl-1,2-naphthoquinone (1c) | $COCH_3$ | 8.25 |
| 3-propionyl-1,2-naphthoquinone (1d) | $COCH_2CH_3$ | 8.23 |
| 3-carbomethoxy-1,2-naphthoquinone (1e) | $COOCH_3$ | 8.20 |
| 3-carboethoxy-1,2-naphthoquinone (1f) | $COOCH_2CH_3$ | 8.18 |
| 3-chloro-1,2-naphthoquinone (1g) | Cl | 7.54[a] |
| 3-bromo-1,2-naphthoquinone (1h) | Br | 7.81[a] |
| 3-methyl-1,2-naphthoquinone (1i) | $CH_3$ | 7.36 |
| 3-ethyl-1,2-naphthoquinone (1j) | $CH_2CH_3$ | 7.24 |
| 3-methoxy-1,2-naphthoquinone (1k) | $OCH_3$ | 6.44 |
| 3-ethoxy-1,2-naphthoquinone (1l) | $OCH_2CH_3$ | 6.42 |

[a] Reference 23.

Table II. Allyltrialkyltin Used in This Work

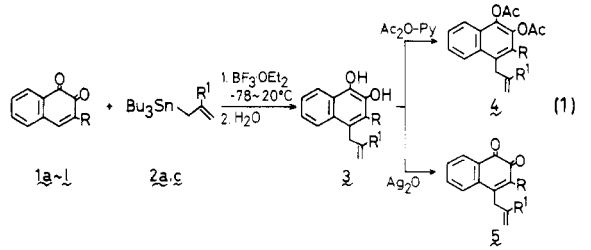


| | $R^1$ | $R^2$ | $R^3$ | $R^4$ |
|---|---|---|---|---|
| 2a | Bu | H | H | H |
| 2b | $CH_3$ | H | H | H |
| 2c | Bu | $CH_3$ | H | H |
| 2d | Bu | H | H | *trans*-$CH_3$ |
| 2e | $CH_3$ | H | H | *trans*-$CH_3$ |
| 2f | Bu | H | $CH_3$ | $CH_3$ |
| 2g | $CH_3$ | H | $CH_3$ | $CH_3$ |

We report herein the details of the reactions of 1,2-naphthoquinones (Table I) with allyltrialkyltins (Table II).

## Results and Discussions

**Reactions of 1,2-Naphthoquinones with Allyl- and (2-Methyl-2-propenyl)tin Reagents.** The allylations were generally accomplished by treatment of 1 equiv of 1,2-naphthoquinone (**1a**) with 1.2 equiv of allyltributyltin (**2a**) or (2-methyl-2-propenyl)tributyltin (**2c**) in the presence of 3 equiv of $BF_3{\cdot}OEt_2$ in dichloromethane under a nitrogen atmosphere at −78 °C, followed by gradual warming (1 h) to room temperature. Since the resulting products, 4-allyl-1,2-naphthalenediol (**3**, R = $R^1$ = H) or 4-(2-methyl-2-propenyl)-1,2-naphthalenediol (**3**, R = H, $R^1$ = $CH_3$), are quite air sensitive and hard to obtain analytically pure, they were converted to their corresponding diacetates (**4**) upon treatment with acetic anhydride–pyridine. They were also converted to the quinones (**5**) by oxidation with silver oxide (eq 1). Other functionalized

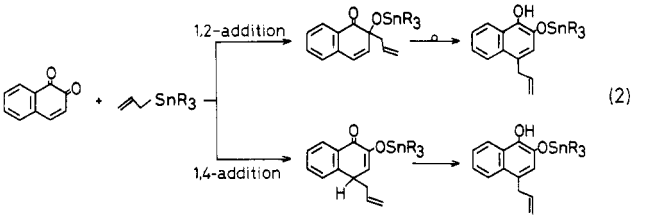


(1)

quinones (**1b–l**) were also converted regioselectively to 4-allylated derivatives upon treatment with **2a** or **2c**. From Table III it is recognized that good to excellent yields of pure products are obtained.

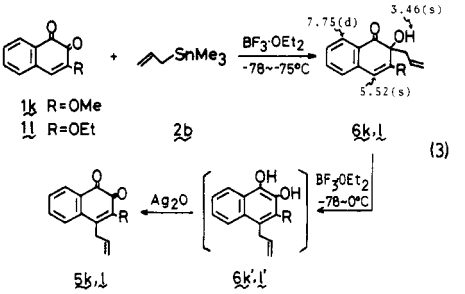
The reaction does not suffer from polar substituents on the quinone nucleus such as nitro, halogen, acyl, and carbalkoxyl groups. This is in marked contrast as compared with the reported reaction of *o*-quinones with (π-allyl)nickel bromide.[3b] The allylation of the quinones with (π-allyl)nickel bromide gave a 2:1 mixture of the mono- and diallylated products, while our method afforded monoallylated derivatives as the products.

Allyltin compounds undergo 1,2-addition to simple ketones,[8a,b] while with α,β-unsaturated ketones only 1,4-addition has been observed.[8b] The latter reaction course, whether the addition occurs to the carbonyl (1,2-addition) or to the enone (1,4-addition), still remains ambiguous (see eq 2).



(2)

To clarify the primary product of the reaction reported here, we first examined the reaction between 3-methoxy-1,2-naphthoquinone (**1k**) and allyltrimethyltin (**2b**). The quinone, **1k**, in dichloromethane was treated with 1.2 equiv of **2b** in the presence of 3 equiv of $BF_3{\cdot}OEt_2$ at −78 °C for 5 min, and then the reaction mixture was quenched by quick addition of saturated aqueous sodium chloride solution. After the organic layer was dried and evaporated, the residue consisted of almost pure 1,2-addition product (**6k**) (NMR analysis). The 1,2-addition product was isolated by preparative layer chromatography on silica gel in 93% yield and showed characteristic signals in its NMR and IR spectra: δ 3.46 (s, 1 H, OH), 5.52 (s, 1 H, ring H), and 7.75 (d, 1 H, peri $H_8$, $J$ = 7 Hz); ν 3490 (OH) and 1680 (C=O) $cm^{-1}$. The allylated quinol (**6k**) smoothly rearranged to **6k′** upon treatment with $BF_3{\cdot}OEt_2$. A calculated amount of $BF_3{\cdot}OEt_2$ was added to a dichloromethane solution of **6k** at −78 °C under a nitrogen atmosphere, and the resulting solution was allowed to warm to 0 °C and then quenched with water. After the usual workup and then oxidation with $Ag_2O$ **5k** was obtained in 87% yield (eq 3).[9] Under the identical conditions, 3-ethoxy-1,2-



(3)

(8) (a) Naruta, Y.; Ushida, S.; Maruyama, K. *Chem. Lett.* **1979**, 919. (b) Hosomi, A.; Iguchi, H.; Endo, M.; Sakurai, H. *Ibid.* **1979**, 979.

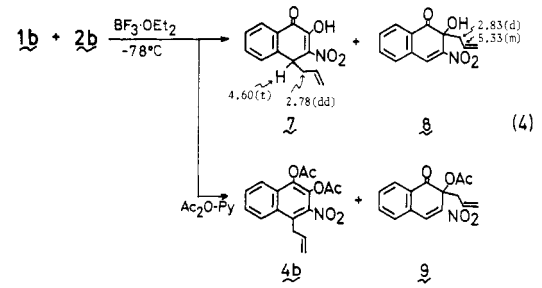
Table III. Reaction of Allyltributyltin and (2-Methyl-2-propenyl)tributyltin with 1,2-Naphthoquinones

| quinone | allyltin | product | yield, % |
|---|---|---|---|
| 1a | 2a | 4-allyl-1,2-naphthalenediol | 78[a] |
| | 2c | 4-(2-methyl-2-propenyl)-1,2-naphthalenediol[b] | 68 |
| 1b | 2a | 4-allyl-3-nitro-1,2-naphthalenediol | 81[a] |
| 1c | 2a | 3-acetyl-4-allyl-1,2-naphthalenediol | 87[a] |
| 1d | 2a | 4-allyl-3-propionyl-1,2-naphthalenediol | 90[a] |
| 1e | 2a | 4-allyl-3-carbomethoxy-1,2-naphthalenediol | 87[a] |
| 1g | 2a | 4-allyl-3-chloro-1,2-naphthoquinone[b] | 89 |
| | 2c | 3-chloro-4-(2-methyl-2-propenyl)-1,2-naphthoquinone[b] | 91 |
| 1i | 2a | 4-allyl-3-methyl-1,2-naphthoquinone[b] | 70 |
| 1k | 2a | 4-allyl-3-methoxy-1,2-naphthoquinone[b] | 95 |
| 1l | 2a | 4-allyl-3-ethoxy-1,2-naphthoquinone[b] | 98 |

[a] Isolated yield of diacetate after acetylation with acetic anhydride–pyridine. [b] Product after oxidation with silver oxide.

naphthoquinone (**1l**) behaved similarly to afforded the 1,2-addition product (**61**, 90%) which rearranged to give **51** (73%). These results strongly suggest that 1,2-addition is the primary process in the reaction of 3-alkoxy-1,2-naphthoquinone with allyltin reagent.

Under the identical conditions, 3-nitro-1,2-naphthoquinone (**1b**) behaved differently from the 3-alkoxy-1,2-naphthoquinones; when **1b** was treated with 1.2 equiv of **2b** in the presence of 3 equiv of $BF_3{\cdot}OEt_2$ at −78 °C for 3 min, both the 1,4-addition product (**7**) and the 1,2-addition product (**8**) (**7**/**8** = 81/19) were produced. NMR (eq 4) for **7**: δ 2.78 (dd, $CH_2$, $J$ = 7 and 5 Hz) and 4.60 (t,




ring H, $J$ = 5 Hz); NMR for **8**: δ 2.83 (d, $CH_2$, $J$ = 7 Hz) and 5.33 (m, CH=C). The spin decoupling method confirmed further these structures; when the double doublet signals at δ 2.78 and the triplet signals at δ 4.60 in **7** were independently irradiated, the signals at δ 4.60 changed to a singlet and the signals at δ 2.78 changed to doublet ($J$ = 7 Hz). The doublet signals at δ 2.83 in **8** changed to singlet when the multiplet signals centered at δ 5.33 were irradiated.

The primary products, **7** and **8**, were too unstable to isolate because of their tendency toward enolization to the corresponding 1,2-diol. A mixture of the crude products was esterified to the corresponding acetyl derivatives to give **4b** and **9** in a respective yield of 63% and 17%. Similarly, in the reaction with **2b**, 3-propionyl-1,2-naphthoquinone (**1d**) gave the 1,4-addition product (79%) and the 1,2-addition product (10%) as the primary products. In contrast to the reaction of 3-alkoxy-1,2-naphthoquinone, both 1,4-addition and 1,2-addition take place simultaneously in the initial stage of the reaction of 3-nitro-1,2-naphthoquinone and 3-propionyl-1,2-naphthoquinone with allyltin reagent.

The differences of the reaction pathways as a function of the nature of the quinone substituents would be worthwhile to study. As discussed above, the electrophilic character of the carbonyl carbon and the $C_4$-carbon in a 1,2-naphthoquinone is one of the factors determining the proportion of 1,4-addition to 1,2-addition products. The methoxyl group in **1k** enhances the electrophilic character of the carbonyl carbon by the inductive effect but exerts the opposite influence on the $C_4$-carbon by the resonance effect. Thus, the electrophilicity of the $C_4$-carbon is consequently greatly diminished. As the result, it has been recognized that 1,2-addition exclusively occurs for **1k**. On the other hand, the nitro group in **1b** strongly enhances the electrophilic character of the $C_4$-carbon by both the resonance and the inductive effects, and also increases that of the carbonyl carbon by the inductive effect. Both 1,4-addition (principal process) and 1,2-addition, therefore, occur for **1b** at the initial stage of the reaction.

A part of our rationalization is in fair agreement with the chemical shift of the proton ($H_4$) attached to the $C_4$-carbon of the 3-substituted 1,2-naphthoquinones: for **1k**, δ 6.44 and for **1b**, δ 8.32. Table I shows that the chemical shift of $H_4$ reflects the electrophilicity of the $C_4$-carbon: the δ value of $H_4$ decreases with the decreasing electrophilic character of the $C_4$-carbon.

Table IV. Reaction of *trans*-2-Butenyltributyltin with 1,2-Naphthoquinones

| quinone | regioisomer ratio[a] α (10) | γ (11) | yield, %[b] | stereochemistry at $\Delta^2$ $E/Z$ of **10**[a] |
|---|---|---|---|---|
| 1a | 78 | 22 | 93 | 95/5 |
| 1b | 9 | 91 | 89 | [c] |
| 1c | 13 | 87 | 89 | 96/4 |
| 1d | 10 | 90 | 96 | 95/5 |
| 1e | 22 | 78 | 92 | [c] |
| 1f | 28 | 72 | 94 | [c] |
| 1g | 46 | 54 | 96 | [c] |
| 1h | 56 | 46 | 74 | 89/11 |
| 1i | 93 | 7 | 75 | [c] |
| 1j | >99 | <1 | 73 | [c] |
| 1k | >99 | <1 | 91 | 80/20 |
| 1l | >99 | <1 | 98 | 77/23 |

[a] Determined by $^1H$ NMR integration of the side chain methyl protons, or by GLC. [b] Isolated yield after acetylation. [c] Not determined.

**Reactions of 1,2-Naphthoquinones with Unsymmetrical Allylic Reagents.** In the addition reaction of unsymmetrical allylic reagents to 1,2-naphthoquinone, the regiochemistry of the introducing allylic moiety (α or γ addition) always becomes an issue. Under the standard conditions, the reaction of **1a** with *trans*-2-butenyltributyltin (**2d**) gave a mixture of α-adduct (**10a**, 78%) and γ-adduct (**11a**, 22%) (eq 5).[10] The regioisomer ratio of α- vs. γ-adduct dramatically changes with the nature of the quinone substituents as summarized in Table IV.

(9) Even in the absence of $BF_3{\cdot}OEt_2$ **6k** rearranged to give **5k** in a low yield (15%). Thus $BF_3{\cdot}OEt_2$ promotes the rearrangement: cf. ref 4c.

(10) In marked contrast in the reaction with 1,4-quinones, 1,2-quinones react with allyltrialkyltin reagents in the absence of $BF_3{\cdot}OEt_2$ to give the allylated products, but in a low yield. However, the addition of $BF_3{\cdot}OEt_2$ into the reaction mixture promotes the reaction giving a higher yield of the products. The details including change of α- vs. γ-product ratio will be given elsewhere.

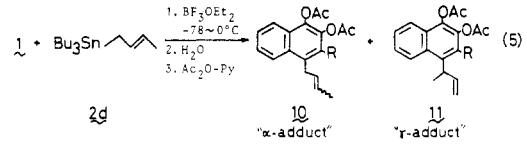
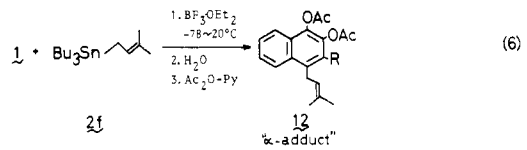
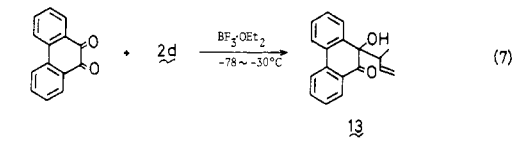



Table IV shows that the introduction of a strong electron-attracting group, such as nitro, alkanoyl, or carbalkoxyl group, in position 3 of the quinone preferentially results in the formation of the γ-adduct. 3-Halogeno derivatives gave nearly equal amounts of the two isomers. Contrary to the effect of the electron-attracting group, 3-alkyl and 3-alkoxyl derivatives gave predominantly or exclusively the α-adduct. Thus, the nature of the substituents in position 3 of 1,2-naphthoquinones remarkably influences the regioisomer ratio.

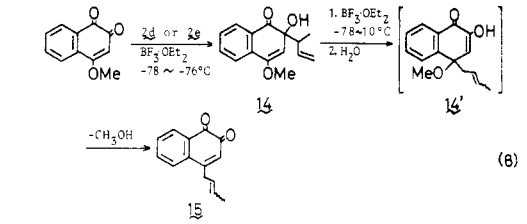
On the contrary, in the reaction with 1,2-naphthoquinones, (3-methyl-2-butenyl)tributyltin (**2f**) showed high regioselectivity to give exclusively α-adduct (**12**) regardless of the substituents on the quinones (eq 6 and Table V).




To examine the orientation of the initial addition of unsymmetrical allylic reagents to quinones, we tried to isolate the corresponding primary products. When 9,10-phenanthrenequinone was treated with *trans*-2-butenyltributyltin (**2d**), the 1,2-addition product (**13**, γ-adduct) was obtained in 95% yield (eq 7). The reaction of 4-




methoxy-1,2-naphthoquinone with **2d** or *trans*-2-butenyltrimethyltin (**2e**) required quenching at low temperature (−78 °C) to isolate the 1,2-addition product (**14**, γ-adduct) (eq 8). Thus, the 1,2-addition of *trans*-2-bute-



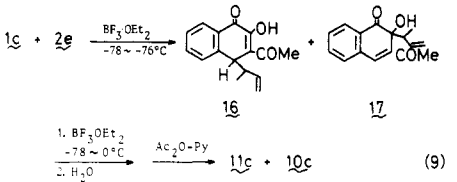

nyltin reagent (crotyltin) occurs at the γ-allyl terminus. To investigate the mode of rearrangement of the 1,2-addition product, $BF_3$·$OEt_2$ was added to a dichloromethane solution of **14** at −78 °C under a nitrogen atmosphere, and the resulting solution was allowed to warm to 10 °C and then quenched with water. After the usual workup, **15** (α-adduct) was exclusively obtained. Overall, conversion of **14** to **15** must invole: (i) Cope rearrangement of the 1,2-addition product to **14'**, and (ii) loss of methanol to give **15** (eq 8).[11] This clearly indicates that the migration of the crotyl group proceeds in the manner of a [3,3]-rearrangement.

On the other hand, when 3-acetyl-1,2-naphthoquinone (**1c**) was treated with **2e** and the resulting solution was quenched within a few minutes at −78 °C, a mixture of the 1,4-addition product, **16** (γ-adduct, 82%), and the 1,2-addition product, **17** (γ-adduct, 10%), was obtained (from NMR). This reaction indicates that 1,4-addition occurs at the γ-allyl terminus of the crotyl moiety. $BF_3$·$OEt_2$ was added to a dichloromethane solution of the mixture of **16** and **17** at −78 °C under a nitrogen atmosphere, and the resulting solution was allowed to warm to 0 °C and then quenched with water. After treatment with acetic anhydride–pyridine **11c** and **10c** were obtained in yields of 82% and 9%, respectively.

Table V. Reaction of (3-Methyl-2-butenyl)tributyltin with 1,2-Naphthoquinones

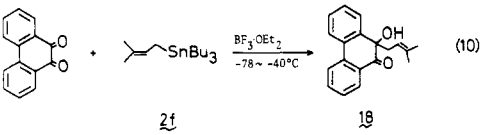
| quinone | product[a,b] | yield, %[c] |
|---|---|---|
| 1a | 12a | 75 |
| 1b | 12b | 83 |
| 1c | 12c | 95 |
| 1g | 12g | 86 |
| 1h | 12h | 92 |
| 1k | *d* | 80[e] |

[a] Product after acetylation with acetic anhydride–pyridine. [b] No γ-adduct was detected by NMR. [c] Isolated yield after acetylation. [d] 3-Methoxy-4-(3-methyl-2-butenyl)-1,2-naphthoquinone. [e] Isolated yield after oxidation with silver oxide.

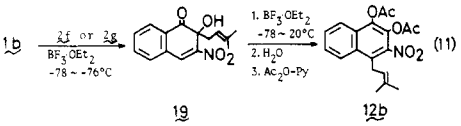



Therefore, α-adduct (**10**) and γ-adduct (**11**) given in eq 5 and Table IV may be produced via different reaction courses: α-adduct is formed via 1,2-addition followed by allyl migration ([3,3]-rearrangement) and γ-adduct is formed via conjugated addition. The product distributions of the α-adduct and the γ-adduct tabulated in Table IV indicate that the regioisomer ratio is governed by the electrophilic character of the $C_4$-carbon of quinones, because the distributions are in good coincidence with the ratio expected from the chemical shift of $H_4$ in Table I. Thus the substituent at position 3 of the quinone controls the pathway as well as the regioisomer ratio in the reaction with *trans*-2-butenyltin reagent.

Contrary to the reaction of *trans*-2-butenyltin reagent, (3-methyl-2-butenyl)tributyltin (**2f**) behaves differently in the regioselectively of the reaction. In the reaction of **2f** with 9,10-phenanthrenequinone, the 1,2-addition product (**18**, α-adduct) was selectively obtained in 50% yield (eq 10). Similarly, when **1b** was treated with **2f** or **2g** and the




resulting solution was quenched within a few minutes, the 1,2-addition product (**19**, α-adduct) was obtained in 48% yield (eq 11). These data show that (i) the initial addition



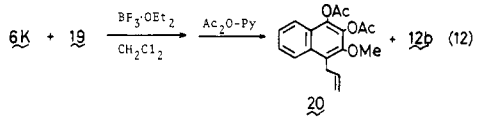

of (3-methyl-2-butenyl)tin reagent (prenyltin) to *o*-quinones occurs in the fashion of 1,2-addition, even for the

(11) Similar processes were reported in the reaction of the masked quinone with allylic bromide: Evans, D. A.; Hoffman, J. M. *J. Am. Chem. Soc.* **1976**, *98*, 1983.

quinone having a powerful electron-attracting group, and (ii) the addition does not always occur at the γ-allyl terminus when the reaction suffers from serious steric difficulties.[4c]

To investigate the mode of rearrangement of **19**, $BF_3$·$OEt_2$ was added to a dichloromethane solution of **19** at −78 °C under a nitrogen atmosphere, and the resulting solution was allowed to warm to room temperature and then quenched with water. After the usual workup, the α-adduct (**12b**, 50%) was exclusively obtained (eq 11). In this case the allyl migration proceeds via [1,3]-sigmatropic rearrangement. The formation of the α-adduct (**12**) indicates that γ-addition of prenyl group, which is more bulky than the crotyl group, is unfavorable because of the steric interactions between C-5 hydrogen (peri $H_5$) and approaching the γ-terminus of the prenyl group. Similar trends of regioselective 1,2-addition (α-adduct) and its [1,3]-rearrangement were reported by Y. Naruta[4c] in the allylation reactions of *p*-quinones with prenyltin reagent. The facile [1,3]-rearrangement in the quinol system by $BF_3$·$OEt_2$ could be interpreted in terms of a "π protonation mechanism".[12]

**The Nature of Allylic Rearrangement.** The allylic migration from the 1,2-addition products to the final products proceeds in the fashion of intramolecular rearrangement as evidenced by results obtained from a cross-over experiment between **6k** and **19**. In the presence of $BF_3$·$OEt_2$, an equimolecular amount of **6k** and **19** was mixed in a dichloromethane solution, and the resulting products were analyzed. No cross-over product was realized (eq 12). This experiment indicates that the allylic




rearrangement from the 1,2-addition products to the final products is of the intramolecular nature.

## Experimental Section

**General Procedures.** All melting points are uncorrected. Proton magnetic resonance spectra were obtained with a JEOL MH-100 spectrometer using tetramethylsilane as an internal standard and the chemical shifts are reported in δ values. Infrared spectra were measured with a Hitachi 215 diffraction grating infrared spectrophotometer. Analytical GLC was performed on a Hitachi 613 gas chromatograph with a flame ionization detector. Analytical and preparative thin-layer chromatography were performed using Merck silica gel HF-254. Satisfactory analytical data (±0.4% for C, H, N) were obtained for all new compounds.

**Materials.** Dichloromethane was freshly distilled. $BF_3$·$OEt_2$ was commercially available and was used without further purification. The following tin reagents were prepared using previously reported methods: allyltributyltin (**2a**),[4c,13] allyltrimethyltin (**2b**),[13] (2-methyl-2-propenyl)tributyltin (**2c**),[4c] *trans*-2-butenyltributyltin (**2d**),[14] *trans*-2-butenyltrimethyltin (**2e**),[13] (3-methyl-2-butenyl)-tributyltin (**2f**),[4c] and (3-methyl-2-butenyl)trimethyltin (**2g**).[4c] 1,2-Naphthoquinone (**1a**, mp 121–122 °C),[15] 3-chloro- (**1g**, mp 171 °C),[16] 3-bromo- (**1h**, mp 164 °C),[17] 3-nitro- (**1b**, mp 156 °C),[18] 3-methyl- (**1i**, mp 121–122 °C),[19] 3-methoxy- (**1k**, mp 185–186 °C),[20] and 4-methoxy-1,2-naphthoquinone (mp 191–192 °C)[20] were prepared according to the methods described in the literature. 3-Acetyl- (**1c**, mp 128–129 °C)[21b] and 3-propionyl-1,2-naphthoquinone (**1d**, mp 105–106 °C) were prepared from the oxidation of the corresponding 3-acyl-1,2-naphthalenediol[21a] by the method of Teuber et al.[20] 3-Carbomethoxy- (**1e**, mp 138–139 °C) and 3-carbethoxy-1,2-naphthoquinone (**1f**, mp 145–146 °C) were prepared by the oxidation of the corresponding 3-carbalkoxy-2-hydroxynaphthalene with Teuber's method.[20] 3-Ethoxy-1,2-naphthoquinone (**1l**, mp 148–149 °C) was prepared by the oxidation of 3-ethoxy-2-naphthol with Fremy's salt.[20] 3-Ethyl-1,2-naphthoquinone (**1j**, mp 97–98 °C) was prepared by the oxidation of 3-ethyl-1,2-naphthalenediol obtained from the Clemmensen reduction of 3-acetyl-1,2-naphthalenediol[21a] by the method of Teuber.[20] 9,10-Phenanthrenequinone was prepared by the method of Underwood.[22]

**General Reaction Procedure.** The reactions between quinones and allyltrialkyltins were all carried out in the following general way. The quinone (0.5 mmol, 1 equiv) was transferred to a 25-mL flask fitted with a rubber serum cap. The flask was filled with nitrogen. After addition of dichloromethane (10 mL), $BF_3$·$OEt_2$ (1.5 mmol, 3 equiv) was added from syringe at −78 °C with constant stirring. The allyltrialkyltin (0.6 mmol, 1.2 equiv) was slowly added from syringe. The reaction mixture was allowed to warm to room temperature (1 h) and then quenched with 5 mL of saturated aqueous NaCl solution, followed by extracting the ether or $CH_2Cl_2$. The organic phase was washed with water, dried over $Na_2SO_4$, and then concentrated in vacuo to yield 1,2-naphthalenediol. The diol was acetylated with acetic anhydride–pyridine or oxidized with silver oxide in ether, and the resulting product was separated and purified by preparative layer chromatography on silica gel (PLC) or by recrystallization.

**Reactions of Allyltrialkyltin (2a, 2b) or (2-Methyl-2-propenyl)tributyltin (2c) with 1,2-Naphthoquinones (eq 1 and Table III). A.** 1,2-Naphthoquinone (79 mg, 0.5 mmol) was treated with allyltributyltin (199 mg, 0.6 mmol) by the general procedure. After acetylation with acetic anhydride–pyridine, isolation by PLC gave 4-allylnaphthalene-1,2-diyl diacetate (**4a**, 112 mg) as needles (from ethanol): mp 123–124 °C; NMR ($CCl_4$) δ 2.32 (s, $OCOCH_3$), 2.45 (s, $OCOCH_3$), 3.82 (d, $CH_2$, $J$ = 8 Hz), 5.04–5.32 (m, C=$CH_2$), 6.00–6.32 (m, CH=C), and 7.20–8.20 (m, aromatic H); IR (KBr) 1760 (vs, C=O), and 1205 (vs) $cm^{-1}$. Anal. ($C_{17}H_{16}O_4$) C, H.

The reaction of **1a** (47.5 mg) with **2c** was undertaken according to the general procedure. After oxidation with $Ag_2O$ in ether, isolation by PLC gave 4-(2-methyl-2-propenyl)-1,2-naphthoquinone (50 mg) as yellow needles (from hexane): mp 110–112 °C; NMR ($CCl_4$) δ 1.83 (s, $CH_3$), 3.32 (s, $CH_2$), 4.82 and 4.92 (each s, C=$CH_2$), 6.20 (s, ring H), and 7.40–8.10 (m, aromatic H); IR (KBr) 1665 (s, C=O) $cm^{-1}$. Anal. ($C_{14}H_{12}O_2$) C, H.

**B.** The reaction of **1b** (61 mg) with **2b** (0.36 mmol) was carried out in the usual fashion. 4-Allyl-3-nitronaphthalene-1,2-diyl diacetate (**4b**, 80 mg) was obtained as pale yellow prism (from ethanol): mp 182–185 °C; NMR ($CDCl_3$) δ 2.33 (s, $CH_3$), 2.45 (s, $CH_3$), 3.85 (d, $CH_2$, $J$ = 7 Hz), 5.05–5.30 (m, C=$CH_2$), 6.02 (m, CH=C), and 7.65–8.30 (m, aromatic H); IR (KBr) 1770 (vs, C=O), 1525 (s, $NO_2$), and 1362 (s, $NO_2$) $cm^{-1}$. Anal. ($C_{17}H_{15}NO_6$) C, H, N.

**C.** The reaction of **1c** (100 mg) with **2a** (0.6 mmol) was undertaken in the usual fashion. 3-Acetyl-4-allylnaphthalene-1,2-diyl diacetate (**4c**, 141 mg) was obtained as white prism: mp 160–163 °C; NMR ($CDCl_3$) δ 2.30 (s, $OCOCH_3$), 2.44 (s, $OCOCH_3$), 2.53 (s, $COCH_3$), 3.80 (d, $CH_2$, $J$ = 8 Hz), 4.90–5.20 (m, C=$CH_2$), 6.26 (m, CH=C), and 7.50–8.23 (m, aromatic H); IR (KBr) 1763 (vs, C=O), and 1692 (s, C=O) $cm^{-1}$. Anal. ($C_{19}H_{18}O_5$) C, H.

**D.** The reaction of **1d** (64 mg) with **2b** (0.3 mmol) was undertaken in the general procedure. 4-Allyl-3-propionylnaphthalene-1,2-diyl diacetate (**4d**, 90 mg) was obtained as col-

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orless prism: mp 113–114 °C; NMR ($CCl_4$) δ 1.17 (t, $CH_3$, $J$ = 8 Hz), 2.20 (s, $OCOCH_3$), 2.36 (s, $OCOCH_3$), 2.75 (q, $COCH_2$, $J$ = 8 Hz), 3.69 (d, $CH_2$, $J$ = 7 Hz), 4.88–5.17 (m, C=$CH_2$), 6.03 (m, CH=C), and 7.35–8.12 (m, aromatic H); IR (KBr) 1765 (vs, C=O), 1695 (s, C=O), 1190 (vs), and 1165 (vs) $cm^{-1}$. Anal. ($C_{20}H_{20}O_5$) C, H.

**E.** The reaction of **1e** (65 mg) with **2a** (0.4 mmol) was undertaken in the usual fashion. 4-Allyl-3-carbomethoxynaphthalene-1,2-diyl diacetate (**4e**, 89 mg) was obtained as a colorless prism from ethanol: mp 159–162 °C; NMR ($CDCl_3$) δ 2.28 (s, $OCOCH_3$), 2.42 (s, $OCOCH_3$), 3.88 (d, $CH_2$, $J$ = 7 Hz), 3.94 (s, $COOCH_3$), 4.95–5.52 (m, C=$CH_2$), 6.00 (m, CH=C), and 7.45–8.28 (m, aromatic H); IR (KBr) 1768 (vs, C=O), 1730 (s, C=O), 1230 (v), and 1200 (vs) $cm^{-1}$. Anal. ($C_{19}H_{18}O_6$) C, H.

**F.** The reaction of **1g** (96 mg) with **2a** (0.6 mmol) was run in the usual manner. 4-Allyl-3-chloro-1,2-naphthoquinone (**5g**, 103 mg) was obtained as orange brown needles from hexane: mp 121–122 °C; NMR ($CDCl_3$) δ 3.82 (d, $CH_2$, $J$ = 7 Hz), 5.20–5.44 (m, C=$CH_2$), 6.00 (m, CH=C), and 7.40–8.20 (m, aromatic H); IR (KBr) 1673 (s, C=O) and 1585 (s) $cm^{-1}$. Anal. ($C_{13}H_9ClO_2$) C, H.

The reaction of **1g** (58 mg) with **2c** (0.36 mmol) was carried out in the general procedure. 3-Chloro-4-(2-methyl-2-propenyl)-1,2-naphthoquinone (67 mg, 91%) was obtained as yellow needles from hexane: mp 113–116 °C; NMR ($CDCl_3$) δ 1.89 (s, $CH_3$), 3.65 (s, $CH_2$), 4.65 and 4.87 (each s, C=$CH_2$), and 7.30–8.20 (m, aromatic H); IR (KBr) 1687 (vs) $cm^{-1}$.

**G.** The reaction of **1i** (52 mg) with **2a** (0.4 mmol) was undertaken in the usual manner. 4-Allyl-3-methyl-1,2-naphthoquinone (**5i**, 44 mg) was obtained as orange needles from hexane: mp 102–103 °C; NMR ($CCl_4$) δ 2.03 (s, $CH_3$), 3.47 (d, $CH_2$, $J$ = 7 Hz), 5.05–5.32 (m, 2 H, C=$CH_2$), 5.96 (m, CH=C), and 7.32–8.14 (m, aromatic H); IR (KBr) 1658 (vs, C=O) $cm^{-1}$. Anal. ($C_{14}H_{12}O_2$) C, H.

**H.** The reaction of **1k** (75 mg) with **2a** (0.48 mmol) was undertaken in the general procedure. 4-Allyl-3-methoxy-1,2-naphthoquinone (**5k**, 86 mg) was obtained as orange red plates from benzene–hexane: mp 120–121 °C; NMR ($CDCl_3$) δ 3.56 (d, $CH_2$, $J$ = 7 Hz), 3.94 (s, $OCH_3$), 5.16–5.36 (m, C=$CH_2$), 5.98 (m, CH=C), and 7.44–8.24 (m, aromatic H); IR (KBr) 1664 (vs, C=O) $cm^{-1}$. Anal. ($C_{14}H_{12}O_3$) C, H.

**I.** The reaction of **1l** (101 mg) with **2a** (0.6 mmol) was carried out in the usual fashion. 4-Allyl-3-ethoxy-1,2-naphthoquinone (**5l**, 118 mg) was obtained as red leaves from benzene–hexane: mp 92–94 °C; NMR ($CDCl_3$) δ 1.38 (t, $CH_3$, $J$ = 7 Hz), 3.60 (d, $CH_2$, $J$ = 8 Hz), 4.16 (q, $OCH_2$, $J$ = 7 Hz), 5.07–5.36 (m, C=$CH_2$), 5.98 (m, CH=C), and 7.27–8.13 (m, aromatic H); IR (KBr) 1672 (vs, C=O) $cm^{-1}$. Anal. ($C_{15}H_{14}O_3$) C, H.

**1,2-Addition Product from the Reaction of Allyltin Reagent with 3-Alkoxy-1,2-naphthoquinone (eq 3). A.** To the $CH_2Cl_2$ solution (10 mL) of **1k** (0.4 mmol) was added $BF_3$·$OEt_2$ (1.2 mmol) under $N_2$ at −78 °C, followed by quick addition of **2b** (0.6 mmol). After 5 min, the reaction mixture was quenched by the addition of saturated aqueous NaCl solution, followed by partitioning with $CH_2Cl_2$. The $CH_2Cl_2$ solution was worked up in the usual manner and evaporated in vacuo. NMR analysis revealed almost pure 2-allyl-5,6-benzo-2-hydroxy-3-methoxycyclohex-3-en-1-one (**6k**). The product was isolated by PLC, developing with chloroform. The $R_f$ 0.53 band contained **6k** (85 mg, 93%) as a yellow oil: NMR ($CCl_4$) δ 2.50 (t, $CH_2$, $J$ = 7 Hz), 3.45 (s, OH), 3.72 (s, $OCH_3$), 4.80–5.00 (m, C=$CH_2$), 5.38–5.78 (m, CH=C), 5.52 (s, ring H), 6.90–7.45 (m, aromatic H), and 7.76 (d, peri $H_8$, $J$ = 7.5 Hz); IR ($CCl_4$) 3490 (m, OH), 1680 (vs, C=O), and 1632 (vs, C=C) $cm^{-1}$.

**B.** The reaction of **1l** (0.3 mmol) with **2a** (0.5 mmol) in the presence of $BF_3$·$OEt_2$ (0.9 mmol) was performed according to the same procedure as described above. After separation by PLC, developing with 1:2 ether–hexane, 2-allyl-5,6-benzo-2-hydroxy-3-ethoxycyclohex-3-en-1-one (**6l**) was obtained (66 mg, 90%) as a yellow oil: NMR ($CCl_4$) δ 1.45 (t, $CH_3$, $J$ = 7 Hz), 2.48 (t, $CH_2$, $J$ = 7 Hz), 3.32 (s, OH), 3.95 (q, $OCH_2$, $J$ = 7 Hz), 4.81–5.02 (m, C=$CH_2$), 5.37–5.78 (m, CH=C), 5.46 (s, ring H), 6.96–7.46 (m, aromatic H), and 7.76 (d, peri $H_8$, $J$ = 7.5 Hz); IR ($CCl_4$) 3500 (w, OH), 1680 (s, C=O), and 1630 (vs, C=C) $cm^{-1}$.

**Rearrangement of the 1,2-Addition Products (eq 3). A.** To the $CH_2Cl_2$ solution of **6k** (85 mg, 0.37 mmol) was added $BF_3$·$OEt_2$ (1.1 mmol) at −78 °C under $N_2$. The resulting solution was allowed to warm to 0 °C, and then quenched with water, followed by partitioning with $CH_2Cl_2$. The $CH_2Cl_2$ solution was dried ($Na_2SO_4$) and concentrated in vacuo. After oxidation with $Ag_2O$, **5k** (80 mg, 87%) was obtained.

**B.** The $CH_2Cl_2$ solution of **6l** (66 mg) was treated with 2 equiv of $BF_3$·$OEt_2$, following the same procedure as for **6k**. The rearrangement product, **5l**, was obtained (48 mg).

**Primary Products from the Reaction of Allyltin Reagent with 1b and 1d (eq 4). A.** To the $CH_2Cl_2$ solution (7 mL) of **1b** (0.3 mmol) was added $BF_3$·$OEt_2$ (0.6 mmol) under $N_2$ at −78 °C, followed by quick addition of **2b** (0.5 mmol). After 3 min, the reaction mixture was quenched by the addition of saturated aqueous NaCl solution, followed by partitioning with $CH_2Cl_2$. The organic layer was worked up in the usual manner and evaporated in vacuo. NMR analysis of the reaction mixture revealed two products: 4-allyl-5,6-benzo-2-hydroxy-3-nitrocyclohex-2-en-1-one (**7**, 81%) and 2-allyl-5,6-benzo-2-hydroxy-3-nitrocyclohex-3-en-1-one (**8**, 19%). **7**: NMR ($CCl_4$) δ 2.78 (dd, $CH_2$, $J$ = 7 and 5 Hz), 4.60 (t, ring H, $J$ = 5 Hz), 4.65 (s, OH), 4.85–5.58 (m, CH=$CH_2$), 7.48–7.80 (m, aromatic H), and 8.03 (d, peri $H_8$, $J$ = 8 Hz). **8**: NMR ($CCl_4$) δ 2.83 (d, $CH_2$, $J$ = 7 Hz), 4.85–5.05 (m, C=$CH_2$), 5.53 (m, CH=C), and 7.40–7.95 (m, aromatic H and OH).

**B.** The reaction of **1b** with **2b** was performed according to the same procedure as described above. After treatment of the reaction mixture with acetic anhydride–pyridine for 1.5 h, the products were separated by PLC, developing with 1:1 ether–hexane. The $R_f$ 0.42 band contained **4b** (62 mg, 63%). The $R_f$ 0.61 band contained 15 mg (17%) of **9** as pale yellow needles from ethanol: mp 152–153 °C; NMR ($CDCl_3$) δ 2.15 (s, $OCOCH_3$), 3.13 (m, $CH_2$), 4.93–5.20 (m, C=$CH_2$), 5.25–5.60 (m, CH=C), 7.57–7.83 (m, aromatic H), 8.18 (s, ring H), and 8.22 (d, peri $H_8$, $J$ = 7 Hz); IR (KBr) 1730 (s, C=O), 1690 (vs, C=O), 1640 (m, C=C), 1518 (s, $NO_2$), and 1325 (s, $NO_2$) $cm^{-1}$. Anal. ($C_{15}H_{13}NO_5$) C, H, N.

**C.** The reaction of **1d** (0.3 mmol) with **2b** (0.6 mmol) in the presence of $BF_3$·$OEt_2$ (0.9 mmol) was performed according to the same procedure as for **1b**. NMR analysis of the reaction mixture revealed two products: 4-allyl-5,6-benzo-2-hydroxy-3-propionylcyclohex-2-en-1-one (1,4-addition product, 79%) and 2-allyl-5,6-benzo-2-hydroxy-3-propionylcyclohex-3-en-1-one (1,2-addition product, 10%). The products were separated by PLC, developing with 2:3 ether–hexane. The $R_f$ 0.72 band contained the 1,4-addition product (55 mg) as pale yellow prisms: mp 100–102 °C dec; NMR ($CCl_4$) δ 1.15 (t, $CH_3$, $J$ = 7 Hz), 2.59 (dd, $CH_2$, $J$ = 6 and 5 Hz), 2.98 (q, $COCH_2$, $J$ = 7 Hz), 4.38 (t, ring H, $J$ = 5 Hz), 4.67–4.96 (m, C=$CH_2$), 5.00–5.22 (m, CH=C), 7.35–7.65 (m, aromatic H), 8.08 (d, peri $H_8$, $J$ = 7 Hz), and 8.40 (s, OH); IR (KBr) 3330 (s, OH), 1640 (vs, C=O) $cm^{-1}$. The $R_f$ 0.55 band contained the 1,2-addition product (8 mg) as an orange oil: NMR ($CCl_4$) δ 1.14 (t, $CH_3$, $J$ = 7 Hz), 2.47 (d, $CH_2$, $J$ = 8 Hz), 2.93 (q, $COCH_2$, $J$ = 7 Hz), 3.85 (s, OH), 4.88–5.15 (m, C=$CH_2$), 5.46–5.76 (m, CH=C), 7.23–7.66 (m, aromatic H), 8.82 (s, ring H), and 8.08 (d, peri $H_8$, $J$ = 7 Hz); IR ($CCl_4$) 3480 (s, OH), 1680 (vs, C=O), and 1640 (s, C=C) $cm^{-1}$.

**Reactions of *trans*-2-Butenyltributyltin with 1,2-Naphthoquinones (eq 5 and Table IV). A.** The tin reagent **2d** (0.6 mmol) was added to **1a** (0.5 mmol) and $BF_3$·$OEt_2$ (1 mmol) in 10 mL of $CH_2Cl_2$, following the general procedure. After acetylation with acetic anhydride–pyridine, the product was isolated by PLC, developing with chloroform. The $R_f$ 0.62 band contained 135 mg of a mixture of two types of allylic isomers, 4-(2-butenyl)naphthalene-1,2-diyl diacetate (**10a**, 78%) and 4-(1-methyl-2-propenyl)naphthalene-1,2-diyl diacetate (**11a**, 22%) as pale brown crystals: mp 51–54 °C: NMR ($CCl_4$) δ 1.50 (d, $CH_3$ of γ-adduct, $J$ = 7 Hz), 1.70 (d, $CH_3$ of α-adduct, $J$ = 6 Hz), 2.15 and 2.25 (each s, $OCOCH_3$ of α and γ-adduct), 3.65 (d, $CH_2$ of α-adduct, $J$ = 7 Hz), 3.96 (m, CH of γ-adduct), 4.95–5.20 (m, C=$CH_2$ of γ-adduct), 5.60 (m, CH=CH of α-adduct), 6.10 (m, CH=C of γ-adduct), and 7.05–8.15 (m, aromatic H of α- and γ-adduct); IR ($CCl_4$) 1770 (vs), 1660 (m), and 1200 (vs) $cm^{-1}$. Anal. ($C_{18}H_{18}O_4$) C, H.

The GLC analysis showed that the $E/Z$ ratio of the α-adduct was 95/5.

**B.** The tin reagent **2d** (0.4 mmol) was added to **1b** (0.3 mmol) and $BF_3$·$OEt_2$ (0.9 mmol) in 7 mL of $CH_2Cl_2$ at −78 °C, following the usual method. The product was isolated by PLC, developing

with 1:1 ether–hexane. The $R_f$ 0.50 band contained 91 mg of a mixture of **10b** (9%) and **11b** (91%) as pale yellow needles: mp 104–108 °C; NMR ($CCl_4$) δ 1.65 (d, $CH_3$ of α- and γ-adduct, $J$ = 7 Hz), 2.29 and 2.42 (each s, $OCOCH_3$ of α- and γ-adduct), 3.70 (m, $CH_2$ of α-adduct), 3.98 (m, CH of γ-adduct), 5.05–5.36 (m, C=$CH_2$ of γ-adduct), 5.53 (m, CH=CH of α-adduct), 6.12 (m, CH=C of γ-adduct), and 7.35–8.38 (m, aromatic H of α- and γ-adduct); IR (KBr) 1780 (vs), 1525 (s), and 1382 (s) $cm^{-1}$. Anal. ($C_{18}H_{17}NO_6$) C, H, N.

**C.** The reaction was carried out in the usual manner using 60 mg of **1c** and 0.4 mmol of **2d**. A mixture of **10c** (13%) and **11c** (87%) was obtained (91 mg, 89%) as colorless needles: mp 113–116 °C; NMR ($CCl_4$) δ 1.65 (m, $CH_3$ of α and γ), 2.27 and 2.42 (each s, $OCOCH_3$ of α and γ) 2.57 (s, $COCH_3$ of α and γ), 3.71 (m, $CH_2$ of α), 3.96 (m, CH of γ), 5.10–5.40 (m, C=$CH_2$ of γ), 5.63 (m, CH=CH of α), 6.35 (m, CH=C of γ), and 7.45–8.37 (m, aromatic H of α and γ); IR (KBr) 1770 (vs), 1700 (s), and 1205 (vs) $cm^{-1}$. Anal. ($C_{20}H_{20}O_5$) C, H.

**D.** The reaction of **1d** (0.3 mmol) with **2d** was undertaken in the general procedure. A mixture (112 mg, 96%) of **10d** (10%) and **11d** (90%) was obtained as colorless prisms: mp 124–128 °C; NMR ($CCl_4$) δ 1.18 (t, $CH_3CH_2$ of α and γ, $J$ = 7 Hz), 1.65 (d, $CH_3$ of α and γ, $J$ = 8 Hz), 2.27 and 2.44 (each s, $OCOCH_3$ of α and γ), 2.84 (q, $CH_2CH_3$ of α and γ, $J$ = 7 Hz), 3.72 (m, $CH_2$ of α), 3.92 (m, CH of γ), 5.12–5.45 (m, C=$CH_2$ of γ), 5.60 (m, CH=CH of α), 6.36 (m, CH=C of γ), and 7.56–8.43 (m, aromatic H of α and γ); IR (KBr) 1775 (vs), 1700 (s), and 1200 (vs) $cm^{-1}$.

**E.** The reaction of **1e** (0.3 mmol) with **2d** (0.36 mmol) was undertaken in the usual fashion. A mixture of **10e** (22%) and 11e (78%) was obtained (98 mg, 92%) as colorless prisms: mp 98–103 °C; NMR ($CCl_4$) δ 1.63 (d, $CH_3$ of α and γ, $J$ = 7 Hz), 2.15 and 2.30 (each s, $OCOCH_3$ of α and γ), 3.73 (m, $CH_2$ of α), 3.75 (s, $OCH_3$ of γ), 3.83 (s, $OCH_3$ of α), 4.05 (m, CH of γ), 5.03–5.30 (m, C=$CH_2$ of γ), 5.53 (m, CH=CH of α), 6.27 (m, CH=C of γ), and 7.35–8.35 (m, aromatic H of α and γ); IR ($CCl_4$) 1780 (vs), 1730 (s), and 1190 (vs) $cm^{-1}$. Anal. ($C_{20}H_{20}O_6$) C, H.

**F.** The reaction of **1f** (115 mg) with **2d** (0.6 mmol) was run in the usual manner. A mixture of **10f** (28%) and **11f** (72%) was obtained (174 mg, 94%) as colorless prisms: mp 100–106 °C; NMR ($CCl_4$) δ 1.35 (t, $CH_3CH_2$ of α and γ, $J$ = 7 Hz), 1.68 (m, $CH_3$ of α and γ), 2.20 and 2.34 (each s, $OCOCH_3$ of α and γ), 3.84 (m, $CH_2$ of α), 4.18 (m, CH of γ), 4.35 (q, $CH_2CH_3$ of γ, $J$ = 7 Hz), 4.38 (q, $CH_2CH_3$ of α, $J$ = 7 Hz), 5.13–5.45 (m, C=$CH_2$ of γ), 5.64 (m, CH=CH of α), 6.35 (m, CH=C of γ), and 7.46–8.49 (m, aromatic H of α and γ); IR ($CCl_4$) 1780 (vs), 1720 (s), and 1190 (vs) $cm^{-1}$.

**G.** The reaction of **1g** (0.3 mmol) with **2d** was carried out in the general procedure. A mixture of **10g** (46%) and **11g** (54%) was obtained (96 mg, 96%) as pale brown crystals: NMR ($CCl_4$) δ 1.65 (m, $CH_3$ of α and γ), 2.35 (s, $OCOCH_3$ of α and γ), 3.95 (m, $CH_2$ of α), 4.80 (m, CH of γ), 5.15–5.35 (m, C=$CH_2$ of γ), 5.60 (m, CH=CH of α), 6.35 (m, CH=C of γ), and 7.40–8.47 (m, aromatic H of α and γ); IR ($CCl_4$) 1780 (vs) and 1190 (vs) $cm^{-1}$. Anal. ($C_{18}H_{17}ClO_4$) C, H.

**H.** The reaction was carried out in the usual manner using 71 mg of **1h** and 0.4 mmol of **2d**. A mixture of **10h** (56%) and **11h** (46%) was obtained (84 mg, 74%) as a pale yellow oil: NMR ($CCl_4$) δ 1.75 (m, $CH_3$ of α and γ), 2.49 (s, $OCOCH_3$ of α and γ), 4.25 (m, $CH_2$ of α), 5.12 (m, CH of γ), 5.45–5.75 (m, C=$CH_2$ of γ), 5.29 (m, CH=CH of α), 6.80 (m, CH=C of γ), and 7.50–8.45 (m, aromatic H of α and γ); IR ($CCl_4$) 1780 (vs) and 1190 (vs) $cm^{-1}$. Anal. ($C_{18}H_{17}BrO_4$) C, H.

The *glc* analysis showed that the $E/Z$ ratio of the α-adduct was 89/11.

**I.** The reaction of **1i** (0.3 mmol) with **2d** (0.4 mmol) was carried out in the usual manner. A mixture of **10i** (93%) and **11i** (7%) was obtained (69 mg, 75%) as a pale yellow oil: NMR ($CCl_4$) δ 1.62 (d, $CH_3$ of α and γ, $J$ = 7 Hz), 2.27 (s, ring $CH_3$ and $OCOCH_3$ of α and γ), 2.33 (s, $OCOCH_3$ of α and γ), 3.78 (m, $CH_2$ of α), 4.42 (m, CH of γ), 5.03–5.28 (m, C=$CH_2$ of γ), 5.52 (m, CH=CH of α), 6.33 (m, CH=C of γ), and 7.30–8.30 (m, aromatic H of α and γ); IR ($CCl_4$) 1778 (vs) and 1200 (vs) $cm^{-1}$. Anal. ($C_{19}H_{20}O_4$) C, H.

**J.** The reaction of **1j** (0.3 mmol) with **2d** (0.4 mmol) was undertaken in the general procedure. The product was isolated by PLC, developing with chloroform. The $R_f$ 0.61 band contained 71 mg (73%) of **10j** as a pale yellow oil: NMR ($CCl_4$) δ 1.19 (t, $CH_3CH_2$, $J$ = 7 Hz), 1.75 (d, $CH_3$, $J$ = 6 Hz), 2.28 (s, $OCOCH_3$), 2.35 (s, $OCOCH_3$), 2.75 (q, $CH_2CH_3$, $J$ = 7 Hz), 3.85 (m, $CH_2$), 5.43 (m, CH=CH), and 7.40–8.24 (m, aromatic H); IR ($CCl_4$) 1775 (vs) and 1200 (vs) $cm^{-1}$. Anal. ($C_{20}H_{22}O_4$) C, H.

**K.** The reaction of **1k** (0.3 mmol) with **2d** (0.36 mmol) was carried out in the usual fashion. The product was isolated by PLC, developing with chloroform. The $R_f$ 0.53 band contained 95 mg (97%) of **10k** as a colorless oil: NMR ($CCl_4$) δ 1.59 (d, *trans*-$CH_3$, $J$ = 6 Hz), 1.81 (d, *cis*-$CH_3$, $J$ = 5 Hz), 2.20 and 2.36 (each s, $OCOCH_3$), 3.68 (m, $CH_2$), 3.78 (s, $OCH_3$), 5.42 (m, CH=CH of cis and trans isomers), and 7.15–7.84 (m, aromatic H); IR ($CCl_4$) 1780 (vs) and 1200 (vs) $cm^{-1}$. Anal. ($C_{19}H_{20}O_5$) C, H.

The NMR spectrum of **10k** showed it to be composed predominantly of the trans isomer of the side chain ($E$:$Z$ = 80:20).

**L.** The reaction of **1l** (60.6 mg) with **2d** (0.4 mmol) was undertaken in the general procedure. The α-adduct (**10l**) was exclusively obtained (100 mg, 98%) as white plates from hexane–benzene: mp 77–78 °C; NMR ($CCl_4$) δ 1.36 (t, $CH_3CH_2$, $J$ = 7 Hz), 1.61 (d, *trans*-$CH_3$, $J$ = 6 Hz), 1.84 (d, *cis*-$CH_3$, $J$ = 5 Hz), 2.24 (s, $OCOCH_3$), 2.30 (s, $OCOCH_3$), 3.75 (m,$CH_2$), 3.95 (q, $OCH_2CH_3$, $J$ = 7 Hz), 5.47 (m, *cis*- and *trans*-CH=CH), and 7.19–7.92 (m, aromatic H); IR (KBr) 1767 (vs) and 1205 (vs) $cm^{-1}$. Anal. ($C_{20}H_{22}O_5$) C, H.

The NMR spectrum of **10l** showed it to be composed predominantly of the trans isomer of the side chain ($E$:$Z$ = 77:23).

**Reactions of (3-Methyl-2-butenyl)tributyltin with 1,2-Naphthoquinones (eq 6 and Table V). A.** The tin reagent **2f** (144 mg, 0.4 mmol) was added to **1a** (0.3 mmol) and $BF_3$·$OEt_2$ (142 mg, 1.0 mmol) in 10 mL of $CH_2Cl_2$, following the general procedure. After acetylation, the product was isolated by PLC, developing with chloroform. The $R_f$ 0.58 band contained 70 mg (75%) of 4-(3-methyl-2-butenyl)naphthalene-1,2-diyl diacetate (**12a**) as a pale yellow oil: NMR ($CCl_4$) δ 1.78 (s, $CH_3$ × 2), 2.23 (s, $OCOCH_3$), 2.35 (s, $OCOCH_3$), 3.72 (d, $CH_2$, $J$ = 7 Hz), 5.42 (t, CH=C, $J$ = 7 Hz), and 7.14–8.04 (m, aromatic H); IR ($CCl_4$) 1770 (s) and 1200 (vs) $cm^{-1}$. Anal. ($C_{19}H_{20}O_4$) C, H.

**B.** The rection of **1b** (0.3 mmol) with **2f** (0.4 mmol) was carried out in the usual manner. The α-adduct (**12b**) was exclusively obtained (89 mg, 83%) as pale yellow crystals: mp 127 °C; NMR ($CDCl_3$) δ 1.70 (s, $CH_3$), 1.83 (s, $CH_3$), 2.28 (s, $OCOCH_3$), 2.42 (s, $OCOCH_3$), 3.70 (d, $CH_2$, $J$ = 7 Hz), 5.13 (m, CH=C), and 7.45–8.10 (m, aromatic H); IR (KBr) 1780 (vs), 1537 (s), 1363 (s), and 1180 (vs) $cm^{-1}$. Anal. ($C_{19}H_{19}NO_6$) C, H, N.

**C.** The reaction of **1c** (0.3 mmol) with **2f** (0.4 mmol) was run in the usual fashion. The α-adduct (**12c**) was obtained exclusively (100 mg, 95%) as a yellow oil: NMR ($CCl_4$) δ 1.82 (s, $CH_3$), 1.92 (s, $CH_3$), 2.37 (s, $OCOCH_3$), 2.53 (s, $OCOCH_3$), 2.65 (s, $COCH_3$), 3.97 (d, $CH_2$, $J$ = 7 Hz), 5.56 (m, CH=C), and 7.95–8.55 (m, aromatic H); IR ($CCl_4$) 1780 (vs), 1705 (s), 1195 (vs), and 1175 (vs) $cm^{-1}$.

**D.** The reaction of **1g** (0.3 mmol) with **2f** (0.4 mmol) was undertaken in the general procedure. The α-adduct (**12g**) was obtained (89 mg, 86%) as white needles: mp 77–79 °C; NMR ($CCl_4$) δ 1.80 (s, $CH_3$), 2.00 (s, $CH_3$), 2.49 (s, $OCOCH_3$), 2.53 (s, $OCOCH_3$), 4.15 (d, $CH_2$, $J$ = 7 Hz), 6.50 (m, CH=C), and 7.80–8.55 (m, aromatic H); IR ($CCl_4$) 1782 (vs) and 1190 (vs) $cm^{-1}$. Anal. ($C_{19}H_{19}ClO_4$) C, H.

**E.** The reaction of **1h** (0.3 mmol) with **2f** (0.4 mmol) was carried out in the usual manner. The α-adduct (**12h**) was obtained (108 mg, 92%) as white needles: mp 84–86 °C; NMR ($CCl_4$) δ 1.68 (s, $CH_3$), 1.87 (s, $CH_3$), 2.23 (s, $OCOCH_3$), 2.25 (s, $OCOCH_3$), 3.95 (d, $CH_2$, $J$ = 7 Hz), 5.12 (m, CH=C), and 7.30–8.00 (m, aromatic H); IR (KBr) 1780 (vs) and 1198 (vs) $cm^{-1}$. Anal. ($C_{19}H_{19}BrO_4$) C, H.

**F.** The reaction of **1k** (0.3 mmol) with **2f** (0.4 mmol) was carried out in the usual manner. After oxidation with silver oxide, 3-methoxy-4-(3-methyl-2-butenyl)-1,2-naphthoquinone was obtained (61 mg, 80%) as dark red needles: mp 78–80 °C; NMR ($CDCl_3$) δ 2.74 (s, $CH_3$), 2.84 (s, $CH_3$), 3.48 (d, $CH_2$, $J$ = 7 Hz), 3.88 (s, $OCH_3$), 5.10 (m, CH=C), and 7.30–8.20 (m, aromatic H); IR (KBr) 1652 (vs) $cm^{-1}$. Anal. ($C_{16}H_{16}O_3$) C, H.

**Reaction of 2d with 9,10-Phenanthrenequinone (eq 7).** The tin reagent **2d** (137 mg, 0.3 mmol) was added to a $CH_2Cl_2$ (15 mL) of the quinone (0.3 mmol) and $BF_3$·$OEt_2$ (0.9 mmol) at −78 °C. The reaction mixture was allowed to warm to −30 °C and then

quenched with saturated aqueous NaCl solution, following the usual workup. The product was isolated by PLC, developing twice with 1:9 ether–hexane. The $R_f$ 0.38 band contained 75 mg (95%) of a mixture of two diastereomers (isomer ratio 38/62) of 9,10-dihydro-9-hydroxy-9-(1-methyl-2-propenyl)-10-oxophenanthrene (**13**) as pale yellow crystals from hexane: mp 61–64 °C; NMR ($CCl_4$) δ 0.80 (d, $CH_3$, $J$ = 7 Hz, 38%), 0.89 (d, $CH_3$, $J$ = 7 Hz, 62%), 2.30 (m, CH), 3.80 (s, OH, 62%), 3.86 (s, OH, 38%), 4.36–4.88 (m, C=$CH_2$), 5.31–5.75 (m, CH=C), and 7.15–7.82 (m, aromatic H); IR (KBr) 3460 (s) and 1680 (vs) $cm^{-1}$.

**1,2-Addition Product and Its Rearrangement in the Reaction of 2d or 2e with 4-Methoxy-1,2-naphthoquinone (eq 8).** The tin reagent **2d** or **2e** (0.4 mmol) was added to a $CH_2Cl_2$ solution of the quinone (0.3 mmol) and $BF_3$·$OEt_2$ (0.6 mmol) under $N_2$ at −78 °C. After stirring for 5 min, the reaction mixture was quenched with saturated aqueous NaCl solution, followed by partitioning with ether. The ethereal solution was worked up in the usual manner and concentrated in vacuo. The product was isolated by quick separation with PLC, developing with chloroform. The $R_f$ 0.34 band contained 17 mg (23%) of a mixture of two diastereomers (isomer ratio 70/30) of 2-hydroxy-5,6-benzo-2-(1-methyl-2-propenyl)-4-methoxycyclohex-3-en-1-one (**14**) as a pale yellow oil: NMR ($CCl_4$) δ 0.87 (d, $CH_3$, $J$ = 7 Hz, 70%), 0.92 (d, $CH_3$, $J$ = 7 Hz, 30%), 2.36 (m, $CH_2$), 3.73 (s, OH, 70%), 3.78 (s, OH, 30%), 3.94 (s, $OCH_3$), 4.05–4.83 (m, C=$CH_2$), 5.37–5.73 (m, CH=C), 5.40 (s, ring H, 30%), 5.43 (s, ring H, 70%), and 7.13–7.70 (m, aromatic H); IR ($CCl_4$) 3440 (OH) and 1645 (C=O) $cm^{-1}$.

To a dichloromethane solution of **14** was added $BF_3$·$OEt_2$ (0.1 mmol) under $N_2$ at −78 °C. The reaction mixture was allowed to warm to 10 °C and then quenched with water. The organic layer was dried and concentrated in vacuo. The product was isolated by quick separation with PLC, developing with benzene. The $R_f$ 0.26 band contained 13 mg (90%) of **15** as orange-yellow prisms from benzene–hexane: mp 124–126 °C; NMR ($CDCl_3$) δ 1.68 (d, $CH_3$, $J$ = 5 Hz), 3.30 (d, $CH_2$, $J$ = 5 Hz), 5.48 (m, CH=CH), 6.23 (s, ring H), 7.30–7.58 (m, aromatic H), and 7.95 (d, peri $H_8$, $J$ = 8 Hz); IR (KBr) 1655 (C=O) $cm^{-1}$.

**Primary Products and Their Rearrangement in the Reaction of 2e with 1c (eq 9).** The tin reagent **2e** (0.5 mmol) was added to a $CH_2Cl_2$ solution of **1c** (0.3 mmol) and $BF_3$·$OEt_2$ (0.9 mmol) at −78 °C. After stirring for a few minutes at −78 °C, the reaction mixture was quenched, followed by partitioning with $CH_2Cl_2$. The $CH_2Cl_2$ solution was worked up in the usual manner and evaporated in vacuo. NMR analysis of the reaction mixture revealed two products: 3-acetyl-5,6-benzo-4-(1-methyl-2-propenyl)-2-hydroxycyclohex-2-en-1-one (**16**, 82%) and 2-hydroxy-5,6-benzo-2-(1-methyl-2-propenyl)-3-acetylcyclohex-3-en-1-one (**17**, 10%). **16**: δ 1.11 (d, $CH_3$, $J$ = 7 Hz), 2.40–2.78 (m, CH), 2.58 (s, $COCH_3$), 4.22 (d, ring H), 4.53–5.12 (m, CH=$CH_2$), 7.25–7.63 (m, aromatic H), 8.05 (d, peri $H_8$, $J$ = 7 Hz), and 8.85 (s, OH). **17**: δ 0.95 (d, $CH_3$, $J$ = 7 Hz), 2.45 (m, CH), 2.62 (s, $COCH_3$), 4.77–5.00 (m, C=$CH_2$), 5.53–5.80 (m, CH=C), 7.32–8.20 (m, aromatic H and ring H), and 8.90 (s, OH).

To a dichloromethane solution of a mixture of **16** and **17** was added $BF_3$·$OEt_2$ under $N_2$ at −78 °C. The reaction mixture was allowed to warm to 0 °C and quenched with water. After the usual workup, **11c** (82%) and **10c** (9%) were obtained.

**Reaction of 2f with 9,10-Phenanthrenequinone (eq 10).** The tin reagent **2f** (0.4 mmol) was added to a $CH_2Cl_2$ solution of the quinone (0.3 mmol) and $BF_3$·$OEt_2$ (0.9 mmol) at −78 °C. The reaction mixture was allowed to warm to −40 °C and then quenched with saturated aqueous NaCl solution, following the usual workup. 9,10-Dihydro-9-hydroxy-9-(3-methyl-2-butenyl)-10-oxophenanthrene (**18**) was obtained (35 mg, 50%) as white prisms: mp 63–64 °C; NMR ($CCl_4$) δ 1.17 (s, $CH_3$), 1.54 (s, $CH_3$), 2.32 (d, $CH_2$, $J$ = 8 Hz), 3.80 (s, OH), 4.84 (t, CH=C, $J$ = 8 Hz), and 7.18–7.82 (m, aromatic H); IR (KBr) 3470 (s) and 1670 (vs) $cm^{-1}$.

**1,2-Addition Product and Its Rearrangement in the Reaction of 2f or 2g with 1b (eq 11).** To a $CH_2Cl_2$ solution (10 mL) of **1b** (0.5 mmol) was added $BF_3$·$OEt_2$ (1 mmol) under $N_2$ at −78 °C, followed by a quick addition of **2g** or **2f** (0.6 mmol). After stirring for 3 min at −78 °C, the reaction mixture was quenched with saturated aqueous NaCl solution, and then extracted with $CH_2Cl_2$. The $CH_2Cl_2$ solution was dried and evaporated in vacuo. The residual oil was triturated with hexane to give 5,6-benzo-2-hydroxy-2-(3-methyl-2-butenyl)-3-nitrocyclohex-3-en-1-one (**19**) as pale yellow crystals (65 mg, 45%): mp 109–110 °C dec; NMR ($CCl_4$) δ 1.48 (s, $CH_3$ × 2), 2.95 (d, $CH_2$, $J$ = 8 Hz), 3.85 (s, OH), 4.78 (t, CH=C, $J$ = 8 Hz), 7.42–7.70 (m, aromatic H), 7.80 (s, ring H), and 8.02 (d, peri $H_8$, $J$ = 7 Hz); IR (KBr) 3480 (m), 1680 (vs), 1510 (s), and 1320 (s) $cm^{-1}$.

$BF_3$·$OEt_2$ (0.4 mmol) was added to a $CH_2Cl_2$ solution (6 mL) of **19** (54.6 mg) under $N_2$ at −78 °C. The resulting solution was allowed to warm to 20 °C and then quenched with water, following the usual method. After acetylation, the product was isolated by PLC, developing with 9:1 ether–hexane. The $R_f$ 0.40 band contained 39 mg (55%) of **12b**.

**Rearrangement of a Mixture of 6k and 19 (eq 12).** $BF_3$·$OEt_2$ (227 mg) was added to a $CH_2Cl_2$ solution of **6k** (89 mg, 0.35 mmol) and **19** (95 mg, 0.35 mmol) at −78 °C under $N_2$. The resulting solution was allowed to warm to 10 °C and then quenched with water. The organic layer was dried and evaporated in vacuo. After acetylation, the products were isolated by PLC, developing with 2:3 ether–hexane. The $R_f$ 0.53 band contained 80 mg (65%) of 4-allyl-3-methoxynaphthalene-1,2-diyl diacetate (**20**) as colorless prisms from ethanol: mp 96–97 °C. Anal. ($C_{18}H_{18}O_5$) C, H. The $R_f$ 0.36 band contained 60 mg (48%) of **12b**. No cross-over product was obtained.

**Registry No.** **1a**, 524-42-5; **1b**, 7474-84-2; **1c**, 75089-88-2; **1d**, 89509-94-4; **1e**, 89509-95-5; **1f**, 89509-96-6; **1g**, 18099-99-5; **1h**, 7474-83-1; **1i**, 31907-43-4; **1j**, 89509-97-7; **1k**, 14557-84-7; **1l**, 89509-98-8; **2a**, 24850-33-7; **2b**, 762-73-2; **2c**, 67883-62-9; **2d**, 35998-93-7; **2e**, 3200-73-5; **2f**, 53911-92-5; **2g**, 17314-40-8; **4a**, 89509-99-9; **4b**, 89510-00-9; **4c**, 89510-01-0; **4d**, 89510-02-1; **4e**, 89510-03-2; **5** (R = H, R′ = $CH_3$), 60404-91-3; **5** (R = Cl, R′ = $CH_3$), 89510-05-4; **5g**, 89510-04-3; **5i**, 89510-06-5; **5k**, 89510-07-6; **5l**, 89510-08-7; **6** (R = $COCH_2CH_3$), 89510-15-6; **6k**, 89510-09-8; **6l**, 89510-10-1; **7**, 89510-11-2; **8**, 89510-12-3; **9**, 89510-13-4; **10a**, 89510-16-7; **10b**, 89510-18-9; **10c**, 89510-20-3; **10d**, 89510-22-5; **10e**, 89510-24-7; **10f**, 89510-26-9; **10g**, 89510-28-1; **10h**, 89510-30-5; **10i**, 89510-32-7; **10j**, 89510-52-1; *cis*-**10k**, 89510-35-0; *trans*-**10k**, 89510-34-9; *cis*-**10l**, 89510-36-1; *trans*-**10l**, 89510-37-2; **11a**, 89510-17-8; **11b**, 89510-19-0; **11c**, 89510-21-4; **11d**, 89510-23-6; **11e**, 89510-25-8; **11f**, 89510-27-0; **11g**, 89510-29-2; **11h**, 89510-31-6; **11i**, 89510-33-8; **12a**, 89510-38-3; **12b**, 89510-39-4; **12c**, 89510-53-2; **12g**, 89510-40-7; **12h**, 89510-41-8; (*R**,*R**)-**13**, 89510-43-0; (*R**,*S**)-**13**, 89510-44-1; (*R**,*R**)-**14**, 89510-45-2; (*R**,*S**)-**14**, 89510-46-3; **15**, 89510-47-4; **16**, 89510-48-5; **17**, 89510-49-6; **18**, 30430-70-7; **19**, 89510-50-9; **20**, 89510-51-0; 4-allyl-5,6-benzo-2-hydroxy-3-propionylcyclohex-2-en-1-one, 89510-14-5; 3-methoxy-4-(3-methyl-2-butenyl)-1,2-naphthoquinone, 89510-42-9.