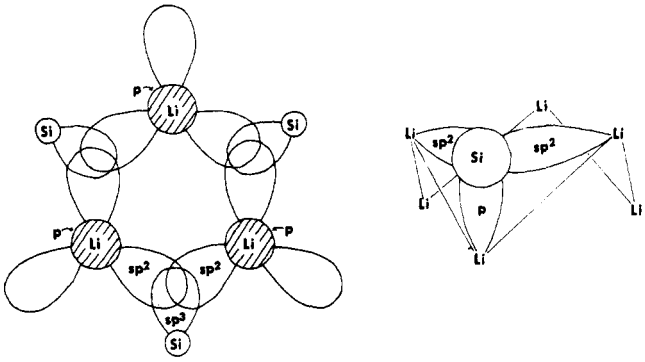


Figure 6. Two views of the trimethylsilyl hexamer depicting the bonding between the bridging silyl group and the lithium atoms.

The marked similarity between this structure and that of cyclohexyllithium hexamer[6] suggests that the metal–hydrogen interactions have little effect on the stereochemistry of these two derivatives, even though Li–H interactions may be present in the cyclohexyl derivative.

The average Li–C distance in a series of organolithium compounds is 2.27 Å (Table SIII[24]) and the corresponding average of all Li–Si distances in trimethylsilyllithium is 2.68 Å. Subtracting the covalent radius of carbon from the average Li–C distance gives an effective radius for lithium of 1.50 Å, whereas from the trimethylsilyl derivative we obtain 1.51 Å. Considering the crudeness of the approximation this suggests that the "effective bonding radius" for lithium in multicentered bonds is 1.5 Å, a value somewhat greater than the radius of lithium observed in Li_2 (1.34 Å); this result is in keeping with the weaker nature of the multicentered interaction.

It appears likely that other silyllithium compounds will have structures similar to that of trimethylsilyllithium in the solid state and in solution and that in the germanium analogues complex structures of a similar nature with Li–Ge distances on the order of 2.7 Å will obtain.

Further work is necessary in the area of the structures of electron-deficient organolithium, silyllithium, and germyllithium compounds to determine the validity of the suggestions proposed, but they do provide a basis from which future studies may be started.

Acknowledgment. This work was supported in part by NSF Grant CHE75-17217; W.H.I. was a Lubrizol Foundation Fellow (1977–1978).

Supplementary Material Available: Listings of observed and calculated structure amplitudes (×10), the calculated atomic coordinates for the hydrogen atoms, a comparison of the Li–Li, Li–C, and Li–S bond distances and of selected Li–C–Li bond angles (Table SIII), and a projection of the trimethylsilyl group on the triangular face of the lithium atoms (17 pages). Ordering information is given on any current masthead page.

References and Notes

(1) T. L. Brown, *Adv. Organomet. Chem.*, **3**, 365 (1965).
(2) J. P. Oliver, *Adv. Organomet. Chem.*, **15**, 235 (1977).
(3) E. Weiss, *J. Organomet. Chem.*, **4**, 101 (1965).
(4) E. Weiss and G. Hencken, *J. Organomet. Chem.*, **21**, 265 (1970).
(5) H. Dietrich, *Acta Crystallogr.*, **16**, 681 (1963).
(6) R. Zerger, W. Rhine, and G. Stucky, *J. Am. Chem. Soc.*, **96**, 6048 (1974).
(7) R. P. Zerger and G. D. Stucky, *J. Chem. Soc., Chem. Commun.*, 44 (1973).
(8) W. H. Ilsley, M. J. Albright, T. J. Anderson, M. D. Glick, and J. P. Oliver, submitted for publication.
(9) R. E. Rundle, *J. Am. Chem. Soc.*, **69**, 1327 (1947).
(10) I. Craubner, *Z. Phys. Chem. (Frankfurt am Main)*, **51**, 225 (1966).
(11) W. E. Rhine, G. Stucky, and S. W. Peterson, *J. Am. Chem. Soc.*, **97**, 6401 (1975).
(12) J. B. Smart, R. Hogan, P. A. Scherr, L. Ferrier, and J. P. Oliver, *J. Am. Chem. Soc.*, **94**, 8371 (1972).
(13) M. A. Ring and D. M. Ritter, *J. Phys. Chem.*, **65**, 182 (1961).
(14) D. F. Gaines and T. V. Iorns, *J. Am. Chem. Soc.*, **89**, 4249 (1967).
(15) A. Tabereaux and R. N. Grimes, *Inorg. Chem.*, **12**, 792 (1973).
(16) T. F. Schaaf, W. Butler, M. D. Glick, and J. P. Oliver, *J. Am. Chem. Soc.*, **96**, 7593 (1974).
(17) T. F. Schaaf and J. P. Oliver, *J. Am. Chem. Soc.*, **91**, 4327 (1969).
(18) W. H. Ilsley, E. A. Sadurski, T. F. Schaaf, M. J. Albright, T. J. Anderson, M. D. Glick, and J. P. Oliver, *J. Organomet. Chem.*, in press.
(19) D. Sayre, *Acta Crystallogr.*, **5**, 60 (1952).
(20) W. Schmonsees, Ph.D. Dissertation, Wayne State University, 1974.
(21) REL, "A Program for Phase Determination by Reiterative Application of Sayre's Equations", R. E. Long, Ph.D. Thesis, University of California, Los Angeles, Calif., 1965, Part III.
(22) Local versions of the following programs were used: (1) SYNCOR, W. Schmonsee's program for data reduction; (2) FORDAP, A. Zalkin's Fourier program; (3) ORFLS and ORFFE, W. Busing, K. Martin, and H. Levy's full-matrix least-squares program and function error programs; (4) ORTEP, C. K. Johnson's program for drawing crystal models. Scattering factors were taken from "International Tables for X-ray Crystallography", Vol. IV, J. A. Ibers and W. C. Hamilton, Eds., Kynoch Press, Birmingham, England, 1974.
(23) Ideal positions for the hydrogens were calculated with the HFINDR program (Zalkin, 1974) as modified by T. J. Anderson and were in reasonable agreement with positions observed on a three-dimensional Fourier difference synthesis.
(24) See paragraph at end of paper regarding supplementary material.
(25) T. L. Brown, D. W. Dickerhoof, and D. A. Bafus, *J. Am. Chem. Soc.*, **84**, 1371 (1962).
(26) W. M. Scovell, B. Y. Kimura, and T. G. Spiro, *J. Coord. Chem.*, **1**, 107 (1971).
(27) K. S. Chen, F. Bertini, and J. K. Kochi, *J. Am. Chem. Soc.*, **95**, 1340 (1973).
(28) J. Hooz, S. Akiyama, F. J. Cedar, M. Bennett, and R. M. Tuggle, *J. Am. Chem. Soc.*, **96**, 274 (1974).
(29) E. Zintl and A. Harder, *Z. Phys. Chem., Abt. B*, **28**, 478 (1935).

Allylation of Quinones with Allyltin Reagents[1]

Yoshinori Naruta

Contribution from the Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606, Japan. *Received September 12, 1979*

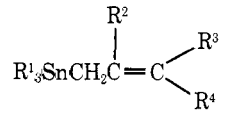
Abstract: Lewis acid (BF_3) catalyzed allylation of quinones with allyl- (**2a**), 2-methyl-2-propenyl- (**2b**), *trans*-2-butenyl- (**2c,d**), 3-methyl-2-butenyl- (**2e,f**), and *trans*-cinnamyltrialkyltin (**2g**) gives the corresponding allylhydroquinones with high regioselectivity. Vitamin $K_{2(5)}$ (**7**) and coenzyme Q_1 (**9**) were prepared in yields of 78 and 75%, respectively. These reactions appear to proceed through allylquinol intermediates which undergo rearrangement under the influence of BF_3. The success of this synthesis of vitamin $K_{2(5)}$ and coenzyme Q_1 depends on the fact that the reaction of 3-methyl-2-butenyltin with quinones occurs at the α carbon of the allylic system.

Introduction

In the past decade there has been considerable interest in the reactions of allyltin compounds[2] because of their marked reactivity toward electrophiles.[3] However, only a few synthetically useful reactions of allyltin reagents have been reported. Trialkylallyltin reagents are easily prepared without

0002-7863/80/1502-3774$01.00/0

Table I. Allyltrialkyltin



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

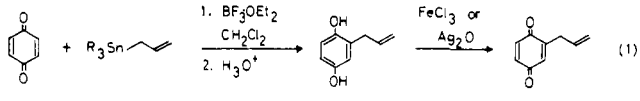
rearrangement from the corresponding allylic halides and they have been shown to react readily with aldehydes and ketones at −78 °C when BF_3 is present.[4] In the present study these tin reagents have been used for the introduction of allylic groups to the quinonoid nucleus. In this way we have succeeded in synthesizing biologically active isoprenyl quinones.[5]

Isoprenylated quinones are widely distributed in nature. They play an important role in several metabolic sequences, e.g., in the electron transport chain, in oxidative phosphorylation, and in abnormal blood clotting. The direct introduction of isoprenyl groups into a quinonoid nucleus is difficult to achieve. The most common method of synthesis of such quinones involves a Friedel–Crafts reaction between a hydroquinone and the appropriate allylic alcohol, followed by mild oxidation to the quinone.[6] However, such preparations suffer from concurrent side reactions such as chromanol formation, ipso substitution, and side-chain cyclization. Despite a number of modifications, e.g., the use of allylic halides, masked quinones, and hybrid Lewis acid catalysts,[7] the reaction remains fundamentally limited by the inherent instability of allylic alcohol components under the acidic conditions employed.[8] Other, more recent, procedures include: (1) the direct reaction of π-allylnickel complexes with quinones, a reaction of limited utility,[9] (2) the well-known coupling of organometallic derivatives with allylic halides,[10d,f] (3) the coupling of aryl bromides with π-allylnickel complexes,[10a-c] and (4) the use of cyanosilylated quinones.[10e] The utility of the last three methods is diminished by the difficulty of preparing the starting materials in cases of biological interest. Mention should also be made of the report that isoprenylation of quinones has been achieved by a free-radical process.[11]

In 1978 we published a preliminary account of the isoprenylation of quinones by the agency of trialkylallyltin reagents.[12a] This paper is concerned with the detailed description of that reaction.

Results and Discussion

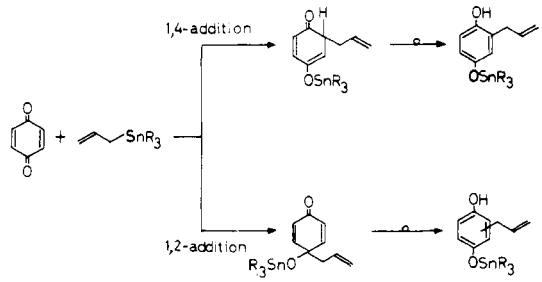
Synthetic Study. The reaction between trialkylallyltins



(Table I) and quinones is initiated at −78 °C and then the system is gradually allowed to warm to room temperature. It will be seen from Table II that good to excellent yields of pure products are obtained. Of particular interest is the fact that this reaction constitutes a direct and efficient synthesis of pure naturally occurring isoprenyl quinones, e.g., coenzyme Q_1 (**9**, 75% yield) and vitamin $K_{2(5)}$ (**7**, 78% yield).

There are four major aspects to these reactions: (a) the Lewis acid employed, (b) the matter of quinol intermediates, (c) regiospecificity as regards the quinol, (d) the question of α vs. γ substitution in the allylic systems. For reasons which will become apparent the second and third of these subjects will be discussed together.

Scheme I

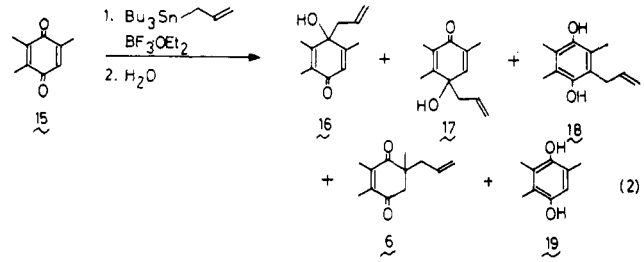


A. The Lewis Acid. In the absence of a Lewis acid the reaction of eq 1 does not occur. A study of the relative utility of BF_3·OEt_2, $TiCl_4$, $AlCl_3$, and $SnCl_4$ revealed that BF_3·OEt_2 and $SnCl_4$ were clearly superior to the other two (Table III).[13] In this work BF_3·OEt_2 was used throughout.

Methylene chloride was routinely employed as the solvent. Experiments employing BF_3·OEt_2 in THF and in Et_2O gave distinctly less satisfactory results; thus, in THF and in Et_2O the product (**4**) was contaminated with complex byproducts.

B. The Matter of Quinol Intermediates and Regiospecificity as Regards the Quinone. Allyltin compounds undergo 1,2 addition to simple ketones.[4b,c] But with α,β-unsaturated ketones only 1,4 addition has been observed.[4c] We have now found that with *o*-quinones and with 9,10-anthraquinones allyltin compounds give exclusively 1,2 addition (Table II, entries 25 and 26). Similarly 2,6-dimethoxybenzoquinone and 2-methoxy-1,4-naphthoquinone provided only one of the possible quinol adducts (entries 22 and 23). These results suggest the possibility of 1,2 addition with *p*-quinones (Scheme I).

When trimethylbenzoquinone reacted with 2 equiv of **2a** in the presence of 5 equiv of BF_3·OEt_2 at −90 to −85 °C for 3 min, followed by quick partitioning of the cold reaction mixture between ether and aqueous saturated NaCl solution, four products were obtained and the yields were estimated by NMR using chloroform as an internal standard. Separation by preparative layer chromatography (PLC) on silica gel gave two quinols, **16** (23%) and **17** (5%), accompanied by enedione **6**



(42%) and allyltrimethylhydroquinone **18** (23%). The quinols, **16** and **17**, showed characteristic NMR spectra and were differentiated by their relative chemical shifts and couplings of the ring methyl and hydrogen signals reported before:[9b] for **16**, δ 1.76 (3 H, J = 1 Hz), 2.00 (6 H), and 5.92 (1 H, J = 1 Hz), respectively, and for **17**, δ 1.86 (6 H), 1.96 (3 H, J = 1 Hz), and 6.50 (1 H, J = 1 Hz), respectively. These allylquinols were stable once purified for several weeks at −30 °C. The isolated yields of **16** and **17** were considerably decreased as compared with those determined by NMR (Table IV). On the other hand, the isolated yields of **6** and **18** were increased. These allylquinols must have rearranged to **6** and **18** in the course of isolation by silica gel PLC. Longer reaction time (5 and 20 min) and higher reaction temperature (−85 to −10 °C) affected the yield of the products: decrease of the yields of **16** and **17** and increase of those of **6** and **18.** These results suggests that these quinols are the primary products in our system.

Table II. Reaction of Allyltin Reagent with Quinones

entry	quinone	allyltin	product	% yield[a]
1	*p*-benzoquinone	**2a**	allylbenzoquinone[b]	85 (66)
2		**2b**	(2-methyl-2-propenyl)benzoquinone[b]	(45)
			p-benzoquinone[b]	(14)
3		**2e**	(3-methyl-2-butenyl)benzoquinone[b]	(55)
4	2,3-dimethylbenzoquinone	**2a**	5-allyl-2,3-dimethylhydroquinone	(72)
			2,3-dimethylhydroquinone	(10)
5		**2e**	5-(3-methyl-1-butenyl)-2,3-dimethylhydroquinone	(62)
6		**2g**	5-(*trans*-cinnamyl)-2,3-dimethylhydroquinone	(81)
7	2,5-dimethylbenzoquinone	**2a**	3-allyl-2,5-dimethylhydroquinone	(90)
8		**2b**	3-(2-methyl-2-propenyl)-2,5-dimethylhydroquinone	99.5 (76)
			5	trace
9		**2e**	3-(3-methyl-2-butenyl)-2,5-dimethylhydroquinone	(82)
10	2,5-dimethylbenzoquinone	**2g**	3-(*trans*-cinnamyl)-2,5-dimethylhydroquinone	(91)
11	2,6-dimethylbenzoquinone	**2a**	2-allyl-3,5-dimethylhydroquinone	(82)
12		**2e**	2-(3-methyl-2-butenyl)-3,5-dimethylhydroquinone	(70)
13		**2g**	2-(*trans*-cinnamyl)-3,5-dimethylbenzoquinone[b]	(49)
			2-(1-phenyl-2-propenyl)-3,5-dimethylbenzoquinone[b]	(32)
14	2,5-di-*tert*-butylbenzoquinone	**2a**	2-allyl-5-*tert*-butylhydroquinone	42 (36)
			2,5-di-*tert*-butylhydroquinone	38 (35)
15		**2e**	2,5-di-*tert*-butylhydroquinone	(88)
16	trimethylbenzoquinone	**2a**	allyltrimethylhydroquinone	44 (37)
			6	54 (54)
17		**2e**	(3-methyl-2-butenyl)trimethylbenzoquinone[b]	68 (65)
18	1,4-naphthoquinone	**2a**	2-allyl-1,4-naphthoquinone[b]	(42)
19	2-methyl-1,4-naphthoquinone	**2e**	vitamin $K_{2(5)}$, **7**[b]	(78)
			8	(18)
20	2,3-dimethoxy-5-methylbenzoquinone	**2a**	2-allyl-3-methyl-5,6-dimethoxybenzoquinone[b]	(61)
21		**2e**	coenzyme Q_1, **9**[b]	(75)
22	2,6-dimethoxybenzoquinone	**2a**	**10**	(52)
23	2-methoxy-1,4-naphthoquinone	**2a**	**11**	(90)
24	1,5-dichloro-9,10-anthraquinone	**2b**	**12**	(95)
25	9,10-phenanthrenequinone	**2a**	**13**	(86)
26	acenaphthenequinone	**2a**	**14**	(91)

[a] Yield in parentheses is isolated yield; others were determined by GLC or NMR. [b] Products after oxidation with silver oxide or ferric chloride.

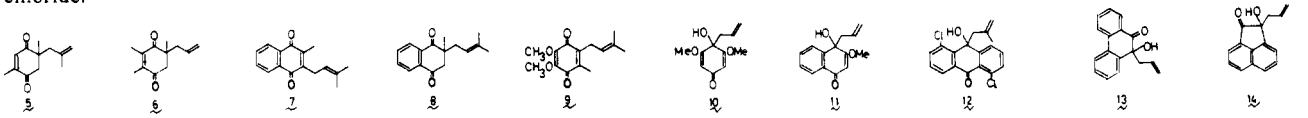


Table III. Effect of Solvents and Lewis Acids on the Reaction of Equation 1[a]

solvent	Lewis acid	Lewis acid/ Quinone	% yield[b] 4	% yield[b] 1
CH_2Cl_2	BF_3·OEt_2	1.0	54[e]	15
		2.0	80	*c*
		3.0	85	*c*
THF		2.0	42[e]	20
Et_2O		2.0	57[e]	*c*
CH_2Cl_2	$TiCl_4$	2.0	53	36
	$AlCl_3$[d]	2.0	29	68
	$SnCl_4$	2.0	73	*c*

[a] All reactions were performed in 1-mmol scale. [b] After oxidation of the reaction mixture with aqueous $FeCl_3$ solution, yield was determined by GLC and NMR. [c] Not detected. [d] Aluminum chloride was added at room temperature and then the tin reagent was added at −78 °C. [e] Accompanied by unassignable complex products.

To clarify the stage of the rearrangement these quinols were separately treated under three different conditions (Table V). Under thermal or protic acid catalyzed conditions, these quinols required several hours for their complete rearrangement, but they underwent rapid convernsion even below −50 °C by BF_3·OEt_2 to give two rearranged products (**6** and **18**). So allylation of trimethylbenzoquinone could occur initially at carbonyl in the fashion of 1,2 addition; then the resulting stannyl ethers of the allylquinols may immediately give the products, **6** and **18.** Allylations of other quinones may take place in a similar fashion.

The effect of BF_3 upon the mode of dienone–phenol rearrangement is worthwhile to study. Under protic acid conditions allylquinol **16** gave **6** (34%) and **18** (60%) at 20 °C. Treatment of the solution of **16** with BF_3·OEt_2 at −70 to 20 °C produced **6** (45%) and **18** (55%). BF_3·OEt_2 slightly promotes [1,2] rearrangement of this quinol. Similarly, quinol **17,** upon treatment with protic acid, gave predominantly **6** (90%) via [3,3] rearrangement. In marked contrast, treatment of **17** with BF_3·OEt_2 produced almost equal amount of **18** (44%, probably via [1,2] rearrangement) and **6** (47%). Thus BF_3·OEt_2 enhances [1,2] rearrangement of allylquinols and increases the production of **18** from **17.** The following experimental results also support this comment. Under the standard reaction conditions, with increasing amount of BF_3·OEt_2, the product ratio (**18**/**6**) monotonously increased, and the proportion of **18** reached 79% when 5 equiv of BF_3·OEt_2 was utilized.

Furthermore, another marked contrast of the present reaction compared with the reported one was exemplified in the allylation of 2,5-dimethylbenzoquinone. Both the reaction with π-allylnickel bromide and that with trimethylsilylcyanide–allyl Grignard reagent[9b] gave solely enedione **5** ([3,3] rearranged product, eq 3a,b). By the present method allylhydroquinone

Table IV. Effect of Reaction Time and Temperature on the Product Distributions of Equation 2[a]

reaction conditions	yield, %[b] 16	17	18	6	19
a, −90 to −85 °C, 3 min	53 (22)	10 (5)	8 (42)	23 (42)	0 (0)
b, −90 to −85 °C, 5 min	41	7	10	41	0
c, −90 to −85 °C, 20 min	41	6	10	41	0
d, −90 to −85 °C, 20 min; then −85 to −10 °C, 30 min	23	0	17	55	5

[a] All reactions were performed in 1-mmol scale in CH_2Cl_2. [b] Yield in parentheses is of isolated product. Others are estimated by NMR using chloroform as an internal standard.

Table V. Rearrangement of Allylquinols **16** and **17**

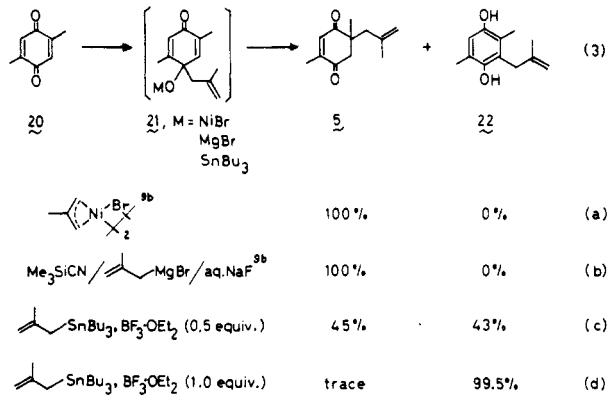
allyl-quinol	reaction conditions	product, % yield[a] 6	18	19	recovery of quinol[a]
16	CH_2Cl_2, reflux, 8 h	0	80	5	0
	2 N HCl/CH_2Cl_2 20 °C, 2 h	11	33	0	55
	20 °C, 6 h	34	60	0	0
	BF_3·OEt_2 (1 equiv)/CH_2Cl_2, −70 to 20 °C, 1 h	45	55	0	0
17	CH_2Cl_2, reflux, 4 h	100	0	0	0
	2 N HCl/CH_2Cl_2 20 °C, 4 h	90	trace	0	0
	BF_3·OEt_2 (0.5 equiv)/CH_2Cl_2, −73 to 25 °C, 1 h	47	44	9	0

[a] Yield was determined by NMR using chloroform as an internal standard.

Table VI. Effect of the Amount of BF_3·OEt_2 on Allylation of Trimethylbenzoquinone[a]

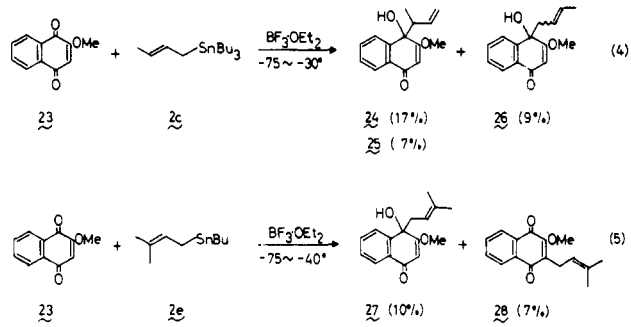
BF_3·OEt_2/ quinone	rel ratio, %[b] 6	18	total yield, %[b]
1.0	64	36	84
2.0	58	43	96
3.0	38	62	99
5.0	21	79	100

[a] All reactions were performed in 1-mmol scale under the standard conditions. [b] Relative ratio and total yield were estimated by NMR integration using $CHCl_3$ as an internal standard.

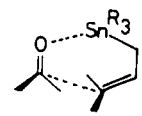


22 was the almost exclusive product (99.5% yield) (probably via [1,2] rearrangement, eq 3d).[14] When the amount of BF_3·OEt_2 was diminished down to 0.5 equiv to that of quinone, then enedione **5** (45% yield) was obtained with a comparable amount of allylhydroquinone **22** (43% yield) (eq 3c). These results support the hypothesis that the amount of BF_3 employed clearly increases the proportion of [1,2] rearrangement pathway against [3,3] one. The facile [1,2] rearrangement in the quinol system by BF_3 could be interpreted in terms of a "π-protonation mechanism".[15]

C. The Question of α vs. γ Substitution on the Allylic Systems. In the addition reaction of unsymmetrical allylic reagents to the carbonyl group, the regioselectivity of the addition (α or γ addition) of the allylic moiety always becomes an issue. To discuss the orientation of primary addition of allyltin reagents to quinones, corresponding quinols were isolated. Under the standard conditions, 2-methoxy-1,4-naphthoquinone (**23**) gave a stable quinol (vide supra). When **23** was treated with **2c** and quenched at −30 °C, three quinols were obtained: two diastereomers (γ adduct), **24** (17%) and **25** (7%), and another isomeric quinol (α adduct), **26** (9%). These isomers were separated by preparative layer chromatography and purified by medium-pressure liquid chromatography. The reaction with **2e** required quenching at lower temperature (−50 °C) to avoid successive reaction, and then α product (**27**, 10%) was isolated accompanied by the rearranged product (**28**, 7%) (eq 5).



In the reaction of allyltin compounds with carbonyl, 1,2 addition inevitably occurred at the γ-allyl terminus.[26] Therefore, this reaction is the first example, to my knowledge, in which the α-addition product has been isolated and characterized. These evidences show that the addition does not always proceed via six-membered transition state such as **29** when it suffers from serious steric difficulties.



29

In the reaction with quinones, crotyltin reagent showed high regioselectively, which depends on the substitutent on *p*-quinones (Table VII): when 2,3 positions of *p*-quinones are free from substituents (e.g., *p*-benzoquinone, 1,4-naphthoquinone, 2,3-dimethylbenzoquinone), it gave predominantly "γ ad-

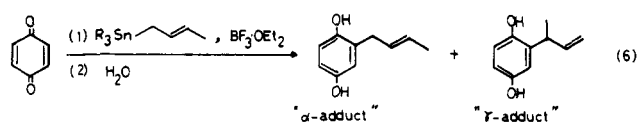


Table VII. Reaction of *trans*-2-Butenyltrialkyltin Reagent with Quinones

quinone	crotyltin	product distribution[a] α adduct, %	product distribution[a] γ adduct, %	stereochemistry[b] of α adduct trans/cis	% yield[c]
p-benzoquinone	**2c**	5	95	*d*	(75)[e]
2,3-dimethylbenzoquinone	**2d**	<1	<99	*d*	70 (41)[f]
2,3-dichlorobenzoquinone	**2d**	37	63	*d*	(88)
1,4-naphthoquinone	**2d**	<1	>99	*d*	(98)[e]
2,5-dimethylbenzoquinone	**2c**	>99	<1	>98/2	(69)
2,6-dimethylbenzoquinone	**2c**	>99	<1	96/4	(25)[g]
2,5-di-*tert*-butylbenzoquinone	**2d**	>99	<1	~70/30	(42)[h]

[a] Determined by NMR integration of the side-chain α proton after oxidation of the corresponding hydroquinone. [b] Determined by NMR integration of the side-chain methyl proton. [c] Yield in parentheses is after isolation; the other is determined by NMR integration using chloroform as an internal standard. [d] Not determined. [e] Isolated yield after oxidation. [f] The corresponding amount of the starting quinone was recovered. [g] Accompanied by 2,6-dimethylbenzoquinone (25%) and 2,6-di(2-butenyl)-3,5-dimethylbenzoquinone (9%). [h] Accompanied by 2,5-di-*tert*-butylhydroquinone (57%).

ducts" ($\gamma/\alpha \geq 95/5$). On the other hand, 2,5- or 2,6-disubstituted quinones (e.g., 2,5-dimethylbenzoquinone or 2,6-dimethylbenzoquinone) exclusively afford "α adducts" ($\alpha/\gamma > 99/1$). This remarkable selectivity may be interpreted in terms of steric interactions between the introduced 2-butenyl group and the ring substituent rather than the stability of allylic cation.[17] A γ addition of these reagents may suffer from rather severe steric interactions between quinone and allylic moieties. Prenyltin compounds (**2e,f**), which are more balky than crotyltin, exclusively afford "α adducts". In appearance, prenyltin reagents react similarly to π-3,3-dimethylallylnickel complex[9b] (not 3,3-dimethylallylmagnesium bromide[10e]) to circumvent the steric interaction mentioned above.

Experimental Section

General. Melting points and boiling points are uncorrected. Proton magnetic resonance spectra were obtained with JEOL PS-100 spectrometer with tetramethylsilane as an internal standard and the chemical shifts are reported in δ values. Infrared spectra were measured on with either JASCO 402G or IRA-1 spectrophotometers. Mass spectra were measured with either Hitachi M-52 or JEOL JMS-01SG-2 mass spectrometers. Analytical GLC was performed on a JEOL JGC-20K gas chromatograph with a flame ionization detector. Liquid chromatography was performed with either 3.9 × 300 mm or 7.0 × 300 mm columns packed with Waters μ-Porasil silica gel. Column chromatography was performed using Wako reagent grade silica gel (100–200 mesh). Analytical and preparative thin layer chromatographs were performed using Merck silica gel F-254. Microanalyses were performed by the Microanalytical Laboratory of Kyoto University, Kyoto, Japan.

Materials. All solvents were freshly distilled and stored under a nitrogen atmosphere. Dichloromethane was distilled from calcium hydride. Ether and THF were distilled from benzophenone ketyl and stored over sodium wire. Tributyltin chloride was distilled at 0.1 mmHg. Trimethyltin bromide was prepared by the method of Kraus.[18] Allyl bromide, *trans*-2-butenyl chloride, and 2-methyl-2-propenyl bromide are commercially available and were used without further purification. 3-Methyl-2-butenyl chloride[19] and cinnamyl bromide[20] were prepared from the corresponding allylic alcohols. 2,3-, 2.5-, and 2,6-dimethylbenzoquinones were prepared from appropriate phenols by the method of Teuber et al.[21] 2,5-Di-*tert*-butylbenzoquinone and trimethylbenzoquinone were prepared by the oxidation of the appropriate hydroquinone following the procedure described by Fieser et al.[22] 2-Methoxy-1,4-naphthoquinone was prepared by the method of Otsuki.[23] 2,6-Dimethoxybenzoquinone was prepared by the method of Ullmann.[24] All other quinones studied are commercially available and were sublimed prior to use. The following tin reagents were prepared using previously reported methods: *trans*-2-butenyltributyltin (**2c**),[25] *trans*-2-butenyltrimethyltin (**2d**).[26] Allyltributyltin (**2a**) was prepared by the coupling reaction of allylmagnesium bromide with tributyltin chloride following the procedure described by Abel et al.[26] $TiCl_4$, $AlCl_3$, $SnCl_4$, and $BF_3{\cdot}OEt_2$ were used without further purification.

(2-Methyl-2-propenyl)tributyltin (2b). This tin reagent was prepared by the coupling reaction of 2-methyl-2-propenylmagnesium bromide with tributyltin chloride following the procedure described by Abel:[26] bp 121–122 °C (4 mm); NMR (CCl_4) δ 0.91 and 1.40 (m, 27 H, 3 C_4H_9), 1.64 (s, 3 H, CH_3), 1.71 (s, 2 H, $CH_2C{=}C$), 4.35 (br, 2 H, $CH_2{=}C$); IR (neat) 2960 (vs), 2920 (vs), 1625 (s, C=C), 1455 (s), 1370 (s), 1270 (s), 850 cm^{-1} (vs, $C{=}CH_2$).

Anal. ($C_{16}H_{33}Sn$) C, H.

(3-Methyl-2-butenyl)tributyltin (2e). This tin reagent was prepared by the reaction of tributyltin lithium[27] with 3-methyl-2-butenyl bromide: bp 114–116 °C (1 mm); NMR (CCl_4) δ 0.90 and 1.4 (m, 29 H, 3 C_4H_9 and CH_2), 1.54 (s, 3 H, *cis*-CH_3), 1.64 (s, 3 H, *trans*-CH_3), 5.14 (t, 1 H, CH=C, J = 8 Hz); IR (neat) 2950 (vs), 2910 (vs), 1665 (w, C=C), 1463 (s), 1377 (s), 1118 (s), 845 cm^{-1} (s).

Anal. ($C_{17}H_{36}Sn$) C, H.

(3-Methyl-2-butenyl)trimethyltin (2f). This tin reagent was prepared by the reaction of trimethyltin lithium[27] with 3-methyl-2-butenyl bromide: bp 56–57 °C (15 mm); NMR (CCl_4) δ 0.06 (2 H, 3 CH_3, $J_{Sn^{117}-H}$ = 50, $J_{Sn^{119}-H}$ = 52 Hz), 1.54 (d, 3 H, *cis*-CH_3, J = 1 Hz), 1.66 (br, 5 H, *trans*-CH_3 and CH_2), 5.22 (m, 1 H, CH=C, J = 1, 8 Hz); IR (neat) 2960 (vs), 2900 (vs), 1445 (s), 1370 (s), 1185 (s), 1120 (vs), 840 (s), 755 cm^{-1} (vs).

Anal. ($C_8H_{18}Sn$) C, H.

***trans*-Cinnamyltributyltin (2g).** This tin reagent was prepared by the coupling reaction of cinnamylmagnesium bromide with tributyltin chloride following a previously described method:[28] bp 163–166 °C (0.4 mm); NMR (CCl_4) δ 0.89 and 1.5 (m, 27 H, 3 C_4H_9), 1.93 (d, 2 H, CH_2, J = 8 Hz), 5.6–6.4 (m, 2 H, CH=CH), 7.09 (m, 5 H, aromatic H); IR (neat) 2925 (vs), 1637 (s, C=C), 1598 (s, ring), 1495 (s, ring), 1463 (s), 1672 (s), 958 cm^{-1} (vs, *trans*-CH=CH).

Anal. ($C_{21}H_{36}Sn$) C, H.

Reaction of Allyltrialkyltin Reagents with Quinones. General Reaction Procedure. The reactions of quinones and allyltrialkyltins were all carried out by the same general procedure. The quinone was placed in a 50-mL two-neck flask fitted with a stopcock and a rubber serum cap. The vessel was alternately evacuated and filled with nitrogen on a vacuum line. After addition of dichloromethane (10 mL), $BF_3{\cdot}OEt_2$ (1 mmol) was added at −78 °C with constant stirring. The allyltrialkyltin (2 mmol) was slowly added from a syringe and warmed to room temperature for about 1–2 h. The reaction mixture was quenched with 30 mL of 2 N HCl and extracted with ether. The ethereal phase was washed with water, then saturated aqueous NaCl, and then dried over $MgSO_4$. After evaporation, products were purified (A) by recrystallization from ether–hexane, or (B) by preparative chromatography on silica gel by eluting with ether–hexane mixture. When isolation of products was either (A) impossible because of their air sensitivity or (B) difficult because of contamination with other products, the reaction mixture was treated with Ag_2O in ether or with aqueous $FeCl_3$ solution; then products were separated and purified by preparative layer chromatography.

Effect of Solvent and Lewis Acid on the Allylation of *p*-Benzoquinone. The reaction of *p*-benzoquinone with **2a** was performed in 1-mmol scale following by the general reaction procedure. After oxidation with aqueous $FeCl_3$, the reaction mixture was evaporated. Products were assigned by comparison with authentic samples and yields were estimated by NMR using *cis*-1,2-dichloroethylene as an internal standard (Table II).

Entry 1. *p*-Benzoquinone (108 mg, 1.0 mmol) was treated with allyltributyltin (662 mg, 2.0 mmol) by the general procedure. After oxidation with aqueous $FeCl_3$ solution, isolation by preparative layer chromatography gave allylbenzoquinone (96 mg, 66%) a brown oil: NMR (CCl_4) δ 2.16 (d, 2 H, CH_2, J = 8 Hz), 5.08 (m, 2 H, C=CH_2), 5.6–6.0 (m, 1 H, CH=C), 6.50 and 6.64 (s, 3 H, ring H); IR (neat) 2970 (s), 1645 (vs, C=O), 1590 (vs), 1450 (s), 1350 (s), 1295 (vs), 1120 (s), 1195 (s), 1010 (vs), 990 (sh), 905 (vs, CH=CH_2), 825 cm^{-1} (s).

Anal. ($C_9H_8O_2$) C, H.

Entry 2. The reaction of *p*-benzoquinone (108 mg) with (2-methyl-2-propenyl)tributyltin (690 mg, 2.0 mmol) was undertaken according to the general reaction procedure. After oxidation by aqueous $FeCl_3$ solution, isolation by preparative layer chromatography gave *p*-benzoquinone (15 mg, 14%) and (2-methyl-2-propenyl)benzoquinone (73 mg, 45%), a brown oil: NMR (CCl_4) δ 1.76 (s, 3 H, CH_3), 3.11 (s, 2 H, CH_2), 4.77 and 4.90 (each s, 2 H, C=CH_2), 6.50 and 6.69 (each s, 3 H, ring H); IR (neat) 3060 (m), 2993 (s), 2943 (s), 1664 (vs, C=O), 1600 (vs), 1447 (s), 1380 (s), 1353 (s),1290 (vs), 1080 (s), 1070 (s), 896 cm^{-1} (vs, C=CH_2); MS *m/e* 162 (P, 98%), 147 (base), 134 (46%), 133 (37%), 119 (59%), 105 (29%), 81 (67%).

Anal. ($C_{10}H_{10}O_2$) C, H.

Entry 3. The reaction of *p*-benzoquinone (108 mg) with (3-methyl-2-butenyl)tributyltin (718 mg, 2.0 mmol) was undertaken in the usual fashion. After oxidation with aqueous $FeCl_3$ solution and isolation by preparative layer chromatography, (3-methyl-2-butenyl)benzoquinone was obtained (98 mg, 55%), yellow crystals: mp 29–30 °C (lit.[29] 30.5 °C); NMR (CCl_4) δ 1.70 (s, 3 H, *cis*-CH_3), 1.80 (s, 3 H, *trans*-CH_3), 3.11 (d, 2 H, CH_2, J = 8 Hz), 5.10 (t, 1 H, CH, J = 8 Hz), 6.52 and 6.76 (each s, 3 H, ring H); IR (neat) 2960 (s), 1668 (vs, C=O), 1600 (vs), 1455 (s), 1395 (s), 1300 (vs), 1100 (s), 970 (s), 955 (s), 890 cm^{-1} (s); MS *m/e* 176 (P, 55%), 161 (base), 147 (28%), 133 (55%), 105 (35%), 94 (20%), 91 (20%), 55 (33%).

Anal. ($C_{11}H_{12}O_2$) C, H.

Entry 4. The reaction of 2,3-dimethylbenzoquinone (136 mg, 1.0 mmol) with allyltributyltin (662 mg) was undertaken in the usual manner. After separation by preparative layer chromatography, 2,3-dimethylhydroquinone (14 mg, 10%) and 5-allyl-2,3-dimethylhydroquinone (130 mg, 72%) were obtained as colorless needles: mp 140.5–141.5 °C; NMR ($CDCl_3$) δ 1.15 (s, 6 H, two ring CH_3), 3.27 (d, 2 H, CH_2, J = 7 Hz), 4.54 (br, 2 H, 2 HO), 5.10 (m, 2 H, C=CH_2), 5.7–6.2 (m, 1 H, CH=C), 6.34 (s, 1 H, ring H); IR (KBr) 3250 (vs, OH), 1643 (m, C=C), 1460 (s), 1420 (s), 1320 (s), 1223 (vs), 1196 (vs), 1108 (m), 1020 (m), 995 and 906 cm^{-1} (m, CH=CH_2); MS *m/e* 178 (P, base), 163 (37%), 135 (26%).

Anal. ($C_{11}H_{14}O_2$), C, H.

Entry 5. The reaction of 2,3-dimethylbenzoquinone (136 mg) with (3-methyl-2-butenyl)tributyltin (718 mg) was undertaken in the usual manner. After separation by preparative layer chromatography, (3-methyl-2-butenyl)-2,3-dimethylhydroquinone (206 mg, 62%) was obtained as white needles: mp 111–112 °C; NMR ($CDCl_3$) δ 1.78 (s, 6 H, 2 CH_3), 2.16 (s, 6 H, 2 ring CH_3), 3.24 (d, 2 H, CH_2, J = 7 Hz), 4.42 (s, 1 H, OH), 4.75 (s, 1 H, OH), 5.24 (t, 1 H, CH=C, J = 7 Hz), 6.40 (s, 1 H, ring H); IR (KBr) 3200 (vs, OH), 1422 (vs), 1212 (vs), 1075 cm^{-1} (vs); MS *m/e* 206 (P, 55%), 189 (60%), 161 (48%), 150 (base), 121 (42%).

Anal. ($C_{13}H_{18}O_2$) C, H.

Entry 6. The reaction of 2,3-dimethylbenzoquinone (136 mg) with *trans*-cinnamyltributyltin (812 mg, 1.0 mmol) was undertaken in the usual manner. After separation by crystallization and purification by recrystallization from ether-hexane, 5-(*trans*-cinnamyl)-2,3-dimethylhydroquinone was obtained as white needles: mp 132–133 °C; NMR ($CDCl_3$) δ 2.14 (s, 6 H, 2 ring CH_3), 3.40 (d, 2 H, CH_2, J = 6 Hz), 4.4 (br, 2 H, 2 HO), 6.39 (m, 3 H, CH=CH and hydroquinone ring H), 7.21 (m, 5 H, aromatic H); IR (KBr) 3330 (vs, OH), 1475 (s), 1325 (s), 1220 (vs), 1075 (vs), 965 cm^{-1} (s, *trans*-CH=CH); MS *m/e* 254 (P, base), 163 (27%), 150 (100%).

Anal. ($C_{17}H_{18}O_2$) C, H.

Oxidation of the hydroquinone by Ag_2O in ether quantitatively gave 5-(*trans*-cinnamyl)-2,3-dimethylbenzoquinone as yellow crystals: mp 61–62 °C; NMR (CCl_4) δ 1.97 (s, 6 H, 2 ring CH_3), 3.27 (d, 2 H, CH_2, J =6 Hz), 6.11 (dt, 1 H, *CH*=CHPh, J = 6, 16 Hz), 6.45 (d, 1 H, CH=*CH*Ph, J = 16 Hz), 6.47 (s, 1 H, quinone ring H), 7.21 (m, 5 H, aromatic H); IR (neat) 1651 (vs, C=O), 1620 (m), 1498 (m), 1451 (m), 1381 (m), 1316 (s), 1270 (m), 970 (s, CH=CH), 783 and 760 (vs), 695 cm^{-1} (s); MS *m/e* 252 (P, base), 237 (50%), 224 (9%), 205 (15%), 181 (11%), 161 (13%), 136 (26%), 121 (40%), 119 (90%), 117 (95%).

The isomeric purity of the side-chain double bond was determined to be all-trans from NMR analysis.

Entry 7. The reaction of 2,5-dimethylbenzoquinone (136 mg) with allyltributyltin (662 mg) was undertaken in the usual manner. After separation by preparative layer chromatography was obtained 3-allyl-2,5-dimethylhydroquinone (160 mg, 90%) as white needles: mp 141–142 °C; NMR ($CDCl_3$) δ 2.16 (s, 6 H, 2CH_3), 3.41 (d, 2 H, CH_2, J = 6 Hz), 4.2 (br, 2 H, 2 HO), 4.8–5.1 (m, 2 H, C=CH_2), 5.7–6.1 (m, 1 H, CH=C), 6.44 (s, 1 H, ring H); IR (KBr) 3240 (vs, OH), 1629 (s, C=C), 1365 (vs), 1209 (vs), 998 and 907 cm^{-1} (m, CH=CH_2); MS *m/e* 178 (P, base), 163 (31%), 135 (25%).

Anal. ($C_{11}H_{14}O_2$) C, H.

Entry 8. The reaction of 2,5-dimethylbenzoquinone (136 mg) with **2b** (690 mg) was undertaken according to the general procedure. After separation by preparative layer chromatography was obtained 3-(2-methyl-2-propenyl)-2,5-dimethylhydroquinone (123 mg, 76%) as colorless needles: mp 117–118 °C; NMR ($CDCl_3$) δ 1.77 (s, 3 H, CH_3C=C), 2.11 and 2.14 (each s, 6 H, 2 ring CH_3), 3.32 (s, 2 H, CH_2), 4.40 (d, 1 H, C=CH, J = 20 Hz), 4.66 (d, 1 H, C=CH, J = 20 Hz), 6.39 (s, 1 H, ring H); IR (KBr) 3320 (vs, OH), 1645 (w), 1440 (s), 1415 (s), 1325 (s), 1230 (vs), 1200 (vs), 1190 (s), 1160 (s), 965 (s), 990 (s), 980 (s), 875 cm^{-1} (s); MS *m/e* 192 (P, base), 177 (52%), 162 (5%), 149 (18%).

Anal. ($C_{12}H_{16}O_2$) C, H.

A trace amount of the enedione **7** was detected by TLC and NMR spectroscopy.

Entry 9. The reaction of 2,5-dimethylbenzoquinone (136 mg) with (3-methyl-2-butenyl)tributyltin (718 mg) was undertaken in the usual manner. After isolation by preparative layer chromatography, 3-(3-methyl-2-butenyl)-2,5-dimethylhydroquinone (169 mg, 82%) was obtained as white needles: mp 153–154 °C; NMR ($CDCl_3$) δ 1.74 (s, 3 H, *cis*-CH_3), 1.82 (s, 3 H, *trans*-CH_3), 2.16 (s, 6 H, 2 ring CH_3), 3.34 (d, 2 H, CH_2, J = 7 Hz), 4.31 and 4.59 (each br, 2 H, 2 HO), 5.18 (t, 1 H, CH=C, J = 7 Hz), 6.41 (s, 1 H, ring H); IR (KBr) 3320 (vs, OH), 2920 (m), 1435 (s), 1320 (vs), 1223 (vs), 1050 (s), 943 (s), 850 cm^{-1} (s); MS *m/e* 206 (P, 94%), 150 (base), 137 (56%), 122 (33%).

Anal. ($C_{13}H_{18}O_2$) C, H.

Entry 10. The reaction of 2,5-dimethylbenzoquinone (272 mg, 2.0 mmol) with *trans*-cinnamyltributyltin (894 mg, 2.2 mmol) in the presence of $BF_3{\cdot}OEt_2$ (2 mmol) in 20 mL of CH_2Cl_2 was performed. After routine isolation, 3-(*trans*-cinnamyl)-2,5-dimethylhydroquinone (462 mg, 91%) was obtained as white needles: mp 125–126 °C; NMR ($CDCl_3$) δ 2.24 (m, 6 H, 2 CH_3), 3.56 (d, 2 H, CH_2, J = 4 Hz), 4.36 (br, 2 H, 2 HO), 6.33 (m, 2 H, CH=CH), 6.47 (s, 1 H, ring H), 7.24 (m, 5 H, aromatic H); IR (KBr) 3370 (vs, OH), 3025 (m), 2920 (m), 1473 (s), 1315 (s), 1220 (s), 1185 (s), 1165 (s), 1075 (s), 950 cm^{-1} (s, *trans*-CH=CH); MS *m/e* 254 (P, 97%), 163 (30%), 150 (base), 138 (28%).

Oxidation of the hydroquinone by Ag_2O in ether gave quantitatively 3-(*trans*-cinnamyl)-2,5-dimethylbenzoquinone as yellow crystals: mp 78–79 °C; NMR (CCl_4) δ 2.02 (m, 6 H, 2 CH_3), 3.34 (d, 2 H, CH_2, J = 7 Hz), 6.00 (m, 1 H, CH_2CH=C, J = 7, 15 Hz), 6.20 (d, 1 H, CH_2CH=C*H*, J = 15 Hz), 6.50 (s, 1 H, ring H), 7.20 (m, 5 H, aromatic H); IR (neat) 3040 (m), 2925 (m), 1640 (vs, C=O), 1610 (s), 1440 (m), 1425 (m), 1375 (s), 1315 (s), 964 (s, *trans*-CH=CH), 780 (s), 750 (s), 685 cm^{-1} (s); MS *m/e* 252 (P, base), 237 (76%), 224 (16%), 209 (17%), 181 (12%), 161 (28%), 91 (48%).

Anal. ($C_{17}H_{16}O_2$) C, H.

The isomeric purity of the side-chain double bond was determined to be all-trans from NMR analysis.

Entry 11. The reaction of 2,6-dimethylbenzoquinone (136 mg) with allyltributyltin (662 mg) was performed in the usual manner. After routine isolation the product was separated by preparative layer chromatography and assigned to be 2-allyl-3,5-dimethylhydroquinone (147 mg, 82%), obtained as white needles: mp 118–119 °C; NMR ($CDCl_3$) δ 2.19 (s, 6 H, 2 CH_3), 3.18 (d, 2 H, CH_2, J = 7 Hz), 4.0 (br, 2 H, 2 HO), 4.8–5.1 (m, 2 H, C=CH_2), 5.6–6.0 (m, 1 H, CH=C), 6.44 (s, 1 H, ring H); IR (KBr) 3260 (vs, OH), 1640 (m), 1462 (s), 1420 (s), 1224 (vs), 1198 (vs), 1110 (s), 997 and 910 cm^{-1} (m, CH=CH_2); MS *m/e* 178 (P, base), 163 (27%), 135 (17%).

Anal. ($C_{11}H_{14}O_2$) C, H.

Entry 12. (3-Methyl-2-butenyl)tributyltin (718 mg, 2.0 mmol) was

added to 2,6-dimethylbenzoquinone (136 mg) and BF_3·OEt_2 (1.0 mmol) in 10 mL of CH_2Cl_2 at −78 °C, following the general reaction procedure. After general isolation the product was separated by preparative layer chromatography. 2-(3-Methyl-3-butenyl)-3,5-dimethylhydroquinone was obtained (231 mg, 70%) as white needles: mp 124–125 °C; NMR ($CDCl_3$) δ 1.68 (d, 3 H, *cis*-CH_3, J = 2 Hz), 1.77 (s, 3 H, *trans*-CH_3), 2.16 (s, 6 H, 2 ring CH_3), 3.20 (d, 2 H, CH_2, J = 7 Hz), 4.2 and 4.5 (each br, 2 H, 2 HO), 5.02 (m, 1 H, CH=C, J = 2, 7 Hz), 6.38 (s, 1 H, ring H); IR (KBr) 3370 (vs, OH), 2920 (s), 1465 (vs), 1332 (vs), 1197 (vs), 1140 (s), 1120 (s), 850 (s), 830 cm^{-1} (s); MS *m/e* 206 (P, 78%), 151 (82%), 137 (base), 123 (25%).

Anal. ($C_{13}H_{18}O_2$) C, H.

Entry 13. *trans*-Cinnamyltributyltin (1.625 g, 4.0 mmol) was added to 2,6-dimethylbenzoquinone (272 mg, 2.0 mmol) and BF_3·OEt_2 (2.0 mmol) in 20 mL of CH_2Cl_2 at −78 °C, following the general reaction procedure. After oxidation with an excess amount of Ag_2O and general isolation, two quinones were separated by preparative layer chromatography, developing with 85:15 hexane–ether. The upper band contained 163 mg (32%) of 2-(1-phenyl-2-propenyl)-3,5-dimethylbenzoquinone, an orange-yellow oil: NMR (CCl_4) δ 1.91 (s, 3 H, ring CH_3), 2.00 (d, 3 H, ring CH_3, J = 1.5 Hz), 5.1–5.3 (m, 2 H, CH=CH_2), 6.3 (m, 1 H, CH=CH_2), 6.51 (q, 1 H, ring H, J = 1.5 Hz), 7.18 (m, 5 H, aromatic H); IR (neat) 3040 (w), 2930 (w), 1653 (vs, C=O), 1614 (m), 1497 (m), 1453 (w), 1380 (m), 1362 (w), 1317 (w), 1260 (s), 1190 (m), 890 cm^{-1} (w); MS *m/e* 252 (P, 33%), 237 (31%), 209 (13%), 181 (7%), 161 (10%), 121 (35%), 119 (94%), 117 (base).

Anal. ($C_{17}H_{16}O_2$) C, H.

The lower band contained 246 mg (49%) of 2-(*trans*-cinnamyl)-3,5-dimethylbenzoquinone, orange-yellow cyrstals: mp 79–81 °C; NMR (CCl_4) δ 1.00 (d, 3 H, ring CH_3, J = 1 Hz), 1.05 (s, 3 H, ring CH_3), 3.30 (d, 2 H, CH_2, J = 6 Hz), 6.00 (m, 1 H, CH=CHPh, J = 6, 16 Hz), 6.38 (d, 1 H, CH=CHPh, J = 16 Hz), 6.47 (q, 1 H, ring H, J = 1 Hz), 7.19 (bs, 5 H, aromatic H); IR (neat) 3035 (m), 2965 (m), 2930 (m), 1650 (vs, C=O), 1620 (s), 1497 (m), 1435 (s), 1380 (s), 1362 (m), 1320 (s), 1287 (m), 1260 (s), 1189 (s), 1100 (m), 1030 (m), 968 (s, *trans*-CH=CH), 913 (m), 886 (m), 750 cm^{-1} (m); MS *m/e* 252 (P, base), 237 (74%), 224 (18%), 209 (27%), 161 (63%), 91 (57%).

Anal. ($C_{17}H_{16}O_2$) C, H.

Entry 14. Allyltributyltin (662 mg, 2.0 mmol) was added to 2,5-di-*tert*-butylbenzoquinone (220 mg, 1.0 mmol) and BF_3·OEt_2 (1 mmol) in 10 mL of CH_2Cl_2 at −78 °C, following the general reaction procedure. After the usual isolation, two hydroquinones were separated by preparative layer chromatography, developing with 1:1 hexane–ether. The upper band contained 95 mg (36%) of 2-allyl-5-*tert*-butylhydroquinone, colorless cubics: mp 118–119 °C; NMR ($CDCl_3$) δ 1.37 (s, 9 H, $(CH_3)_3$), 3.27 (d, 2 H, CH_2, J = 7 Hz), 4.60 and 4.67 (each s, 2 H, 2 HO), 5.10 (m, 2 H, C=CH_2), 5.7–6.1 (m, 1 H, CH=C), 6.38 (s, 2 H, ring H); IR (KBr) 3300 (vs, OH), 1643 (m, C=C), 1415 (vs), 1188 (vs), 996 and 908 cm^{-1} (m, CH=CH_2), MS *m/e* 206 (P, 64%), 191 (base), 163 (18%), 150 (17%).

Anal. ($C_{13}H_{18}O_2$) C, H.

The lower band contained 78 mg (35%) of 2,5-di-*tert*-butylhydroquinone.

Entry 15. (3-Methyl-2-butenyl)tributyltin (718 mg, 2 mmol) was added to 2,5-di-*tert*-butylbenzoquinone (220 mg, 1.0 mmol) and BF_3·OEt_2 (1 mmol) in 10 mL of CH_2Cl_2, following the general reaction procedure. After usual isolation, 2,5-di-*tert*-butylhydroquinone (195 mg, 88%) was obtained.

Entry 16. Allyltributyltin (662 mg) was added to trimethylbenzoquinone (154 mg, 1.0 mmol) and BF_3·OEt_2 (1 mmol) in 10 mL of CH_2Cl_2, following the general reaction procedure. After usual isolation, two products were separated by preparative layer chromatography, developing with 1:1 hexane–ether. The lower band contained 72 mg (37%) of allyltrimethylhydroquinone (**19**), colorless needles: mp 140–142 °C; NMR ($CDCl_3$) δ 1.15 (s, 9 H, $(CH_3)_3$), 3.38 (d, 2 H, CH_2, J = 7 Hz), 4.2 and 4.3 (each br, 2 H, 2 HO), 4.8–5.0 (m, 2 H, C=CH_2), 5.7–6.0 (m, 1 H, CH=C); IR (KBr) 3260 (vs, OH), 1638 (m, C=C), 1240 (vs), 1075 (s), 990 and 902 cm^{-1} (s, CH_2=CH); MS *m/e* 192 (P, base), 177 (26%), 162 (8%), 149 (13%), 42 (7%).

Anal. ($C_{12}H_{16}O_2$) C, H.

The upper band contained 103 mg (54%) of 5-allyl-2,3,5-trimethylcyclohex-2-ene-1,4-dione (**8**), a pale yellow oil: NMR ($CDCl_3$) δ 1.19 (s, 3 H, CH_3), 1.98 (s, 6 H, 2 CH_3), 2.23 (q, 1 H, diastereotopic CH_2C=C, J = 7, 14 Hz), 2.38 (q, 1 H, diastereotopic CH_2C=C, J = 7, 14 Hz), 2.57 (d, 1 H, diastereotopic ring CH_2, J = 16 Hz), 2.84 (d, 1 H, diastereotopic ring CH_2, J = 16 Hz), 5.00 (m, 2 H, C=CH_2), 5.4–5.9 (m, 1 H, CH=C); IR (neat) 2985 (s), 2925 (s), 1670 (vs, C=O), 1375 (s), 1305 (s), 1255 (s), 995 and 915 cm^{-1} (m, CH=CH_2).

Anal. ($C_{12}H_{16}O_2$) C, H.

Entry 17. The tin reagent **2e** (718 mg) was added to trimethylbenzoquinone (154 mg) and BF_3·OEt_2 (1 mmol) in 10 mL of CH_2Cl_2, following the general reaction procedure. After oxidation with an excess amount of Ag_2O in ether and then isolation as in the usual method, two quinones were separated by preparative layer chromatography, developing with 85:15 hexane–ether. The upper band contained 142 mg (65%) of (3-methyl-2-butenyl)trimethylbenzoquinone, a yellow oil: NMR (CCl_4) δ 1.68 (s, 3 H, *cis*-CH_3), 1.74 (s, 3 H, *trans*-CH_3), 1.96 (s, 9 H, 3 ring CH_3), 3.12 (d, 2 H, CH_2, J = 8 Hz), 4.88 (t, 1 H, CH=C, J = 8 Hz); IR (neat) 2920 (s), 1635 (vs, C=O), 1435 (s), 1370 (s), 1300 (s), 1255 cm^{-1} (s).

Anal. ($C_{14}H_{18}O_2$) C, H.

The lower layer contained 46 mg (30%) of trimethylbenzoquinone.

Entry 18. The tin reagent **2a** (662 mg) was added to 1,4-naphthoquinone (158 mg, 1.0 mmol) and BF_3·OEt_2 (1.0 mmol) in 10 mL of CH_2Cl_2, following the general reaction procedure. After oxidation with an excess amount of aqueous $FeCl_3$ solution and then isolation as in the usual method, a quinone was separated by preparative layer chromatography, developing with 80:20 hexane–ether. Allyl-1,4-naphthoquinone was obtained 83 mg (42%), yellow crystals: mp 44–45 °C; NMR ($CDCl_3$) δ 3.28 (d, 2 H, CH_2, J = 7 Hz), 5.0–5.3 (m, 2 H, C=CH_2), 5.6–6.0 (m, 1 H, CH=C), 6.66 (s, 1 H, ring H), 7.5–7.7 (m, 2 H, aromatic H), 7.8–8.0 (m, 2 H, aromatic H); IR (KBr) 1662 (vs, C=O), 1623 (s), 1590 (s), 1408 (s), 1330 (vs), 1296 (vs), 1240 (vs), 1140 (s), 917 cm^{-1} (vs).

Anal. ($C_{13}H_{10}O_2$) C, H.

Entry 19. The tin reagent **2f** (280 mg, 1.2 mmol) was added to 2-methyl-1,4-naphthoquinone (172 mg, 1.0 mmol) and BF_3·OEt_2 (3.0 mmol) in 10 mL of CH_2Cl_2, following the general procedure. After oxidation with Ag_2O in ether, products were separated by preparative layer chromatography, developing with 80:20 hexane–ether. The upper band contained vitamin $K_{2(5)}$ (**9**, 189 mg, 78%), a yellow oil; NMR (CCl_4) δ 1.68 (s, 3 H, *cis*-CH_3), 1.70 (s, 3 H, *trans*-CH_3), 2.16 (s, 3 H, ring CH_3), 3.28 (d, 2 H, CH_2, J = 7 Hz), 5.00 (t, 1 H, CH=C, J = 7 Hz), 7.62 (m, 2 H, aromatic H), 7.96 (m, 2 H, aromatic H); IR (neat) 2960 (s), 2910 (s), 1645 (vs, C=O), 1610 (s), 1590 (vs), 1430 (s), 1370 (s), 1325 (s), 1290 (vs), 965 (s), 780 (s), 705 cm^{-1} (vs); MS *m/e* 240 (P, 38%), 225 (53%), 212 (25%), 199 (36%), 175 (44%), 154 (72%), 143 (49%), 110 (base).

Anal. ($C_{16}H_{16}O_2$) C, H.

The lower band contained 2,3-benzo-6-methyl-6-(3-methyl-2-butenyl)cyclohexane-1,4-dione (**10**, 44 mg, 18%), a pale yellow oil: NMR (CCl_4) δ 1.24 (s, 3 H, ring CH_3), 1.52 (s, 3 H, *cis*-CH_3), 1.64 (s, 3 H, *trans*-CH_3), 2.20 (q, 1 H, diastereotopic CH_2C=C, J = 8, 14 Hz), 2.43 (q, 1 H, diastereotopic CH_2C=C, J = 8, 14 Hz), 2.69 (d, 1 H, diastereotopic ring CH_2, J = 16 Hz), 2.94 (d, 1 H, diastereotopic ring CH_2, J = 16 Hz), 5.00 (t, 1 H, CH=C, J = 8 Hz), 7.66 (m, 2 H, aromatic H), 7.98 (m, 2 H, aromatic H); IR (neat) 2960 (s), 2920 (s), 1680 (vs, C=O), 1590 (vs), 1290 (vs), 1250 (vs), 1210 (s), 975 (s), 750 cm^{-1} (s); MS *m/e* 242 (P, 11%), 227 (12%), 174 (52%), 145 (28%), 144 (41%), 138 (28%), 110 (base), 97 (33%).

Anal. ($C_{16}H_{18}O_2$) C, H.

Entry 20. The tin reagent **2a** (662 mg) was added to 2,3-dimethoxy-5-methylbenzoquinone (182 mg, 1.0 mmol) and BF_3·OEt_2 (1.0 mmol), following the general reaction procedure. After oxidation with aqueous $FeCl_3$ solution and then isolation by preparative layer chromatography (developing twice with 80:20 hexane–ether), 2-allyl-5,6-dimethoxy-3-methylbenzoquinone (136 mg, 61%) was obtained, a red oil: NMR (CCl_4) δ 1.98 (s, 3 H, ring CH_3), 3.17 (d, 2 H, CH_2C=C, J = 6 Hz), 3.95 (s, 6 H, 2 CH_3O), 4.88–5.13 (m, 2 H, C=CH_2), 5.47–5.94 (m, 1 H, CH=C); IR (neat) 2945 (s), 1660 (vs, C=O), 1615 (vs), 1454 (s), 1284 (m), 1252 (vs), 1200 (s), 1157 (s), 1095 (s), 1070 (s), 1003 (s), 915 cm^{-1} (m); MS *m/e* 222 (P, base), 207 (57%), 179 (30%), 151 (32%), 123 (36%).

Anal. ($C_{12}H_{14}O_4$) C, H.

Entry 21. The allyltin **2e** (718 mg, 2.0 mmol) was added to 2,3-dimethoxy-5-methylbenzoquinone (182 mg, 1.0 mmol) and BF_3·OEt_2 (1.0 mmol) in 10 mL of CH_2Cl_2, following the general procedure.

After routine isolation and then oxidation with aqueous $FeCl_3$ solution, isolation by preparative layer chromatography developing twice with 80:20 hexane-ether provided coenzyme Q_1 (**11,** 189 mg, 75%), a red oil: NMR (CCl_4) δ 1.66 (s, 3 H, *cis*-CH_3), 1.73 (s, 3 H, *trans*-CH_3), 1.96 (s, 3 H, ring CH_3), 3.09 (d, 2 H, CH_2, J = 7 Hz), 3.92 (s, 6 H, 2 CH_3O), 4.84 (t, 1 H, CH=C, J = 7 Hz); IR (neat, 2930 (vs), 1650 (vs, C=O), 1617 (vs, ring C=C), 1455 (vs), 1329 (s), 1262 (vs), 1155 (vs), 1102 (s), 1013 (s), 938 (m), 836 cm^{-1} (m); MS *m/e* 250 (P, 11%), 235 (base), 207 (9%), 203 (11%), 120 (21%), 118 (63%), 116 (68%).

Anal. ($C_{14}H_{18}O_4$) C, H.

Entry 22. The allyltin **2a** (662 mg) was added to 2,6-dimethoxybenzoquinone (168 mg, 1.0 mmol) and BF_3·OEt_2 (1 mmol) in 20 mL of CH_2Cl_2, following the general reaction procedure. After evaporation of ethereal extract in vacuo, residual precipitate was recrystallized from hexane-ether to give 1-allylcyclohexa-2,5-dien-4-oxo-1-ol (**12,** 111 mg, 52%), colorless needles: mp 107–108 °C; NMR ($CDCl_3$) δ 2.74 (d, 2 H, CH_2, J = 7 Hz), 3.72 (s, 6 H, 2 CH_3O), 4.8–5.0 (m, 2 H, C=CH_2), 5.1–5.3 (m, 1 H, CH=C), 5.36 (s, 2 H, ring H); IR (KBr) 3200 (s, OH), 1660 (vs, C=O), 1597 (vs), 1375 (vs), 1237 (vs), 1210 (vs), 1150 (s), 1045 (s), 1005 and 915 cm^{-1} (m, CH=CH_2); MS *m/e* 210 (P, 34%), 172 (22%), 168 (base), 153 (26%).

Anal. ($C_{11}H_{14}O_4$) C, H.

Entry 23. The allyltin **2a** (662 mg) was added to 2-methoxy-1,4-naphthoquinone (188 mg, 1.0 mmol) and BF_3·OEt_2 (1.0 mmol) in 20 mL of CH_2Cl_2, following the general reaction procedure. After evaporation of the ethereal extract in vacuo, precipitated material was recrystallized from hexane-ether to give 1-allyl-2,3-benzo-1-hydroxy-6-methoxycyclohex-5-en-4-one (**13,** 205 mg, 88%), white crystals: mp 144–145 °C; NMR ($CDCl_3$) δ 2.74 (br, 1 H, OH), 2.74 (d, 1 H, diastereotopic CH_2, J = 8 Hz), 2.78 (d, 1 H, diastereotopic CH_2, J = 8 Hz), 3.80 (s, 3 H, CH_3O), 4.7–4.9 (m, 2 H, C=CH_2), 4.9–5.2 (m, 1 H, CH=C), 5.64 (s, 1 H, ring H), 7.2–7.8 (m, 3 H, aromatic H), 8.00 (m, 1 H, aromatic H); IR (KBr) 3290 (vs, OH), 1638 (vs, C=O), 1597 (vs, ring), 1360 (vs), 1230 (vs), 1015 (vs), 996 and 926 cm^{-1} (s, CH=CH_2); MS *m/e* 230 (P, 3%), 224 (4%), 188 (base), 167 (10%), 129 (6%), 105 (7%).

Anal. ($C_{14}H_{14}O_3$) C, H.

Entry 24. The tin reagent **2b** (690 mg, 2.0 mmol) was added to 1,5-dichloro-9,10-anthraquinone (227 mg, 1.0 mmol) and BF_3·OEt_2 (1.0 mmol) in 20 mL of CH_2Cl_2 at −30 °C, following the general reaction procedure. After evaporation of ethereal extract in vacuo, precipitated crystals were recrystallized from hexane-CH_2Cl_2 to give 1,5-dichloro-9-(2-methyl-2-propenyl)-9-hydroxy-10-oxoanthracene (**14,** 263 mg, 100%), pale yellow needles; mp 132–133 °C; NMR ($CDCl_3$) δ 1.00 (s, 3 H, CH_3), 2.66 (d, 1 H, diastereotopic CH_2, J = 12 Hz), 3.22 (d, 1 H, diastereotopic CH_2, J = 12 Hz), 3.84 (m, 2 H, CH=C and OH), 4.56 (m, 1 H, CH=C), 7.3–8.2 (m, 6 H, aromatic H); IR (KBr) 3300 (vs, OH), 1658 (vs, C=O), 1585 (vs), 1430 (vs), 1139 (vs), 897 cm^{-1} (m, C=CH_2); MS *m/e* 279 (64%), 277 (base). Anal. ($C_{18}H_{14}O_2Cl_2$) C, H, Cl.

Entry 25. The allyltin **2a** (331 mg, 1.0 mmol) was added to 9,10-phenanthrenequinone (104 mg, 0.5 mmol) and BF_3·OEt_2 (1.0 mmol) in 5 mL of CH_2Cl_2 at −78 °C, followed the general procedure. After evaporation of ethereal extract in vacuo, residual precipitate was recrystallized from hexane-ether to give 9-allyl-9-hydroxy-10-oxaphenanthrene (**15,** 108 mg, 86%), pale yellow crystals: mp 44–46 °C; NMR (CCl_4) δ 2.39 (m, 2 H, CH_2), 4.00 (s, 1 H, OH), 4.6–5.0 (m, 2 H, C=CH_2), 5.3–5.8 (m, 1 H, CH=C), 7.1–7.9 (m, 8 H, aromatic H); IR (neat) 3450 (s, OH), 3040 (m), 2890 (m), 1692 (vs, C=O), 1642 (vs), 1603 (m), 1482 (vs), 1285 (s), 1235 (s), 1205 (s), 1023 (s), 924 cm^{-1} (vs).

Anal. ($C_{17}H_{14}O_2$) C, H.

Entry 26. The allyltin **2a** (662 mg) was added to acenaphthenequinone (182 mg, 1.0 mmol) and BF_3·OEt_2 in 20 mL of CH_2Cl_2 at −78 °C, following the general reaction procedure. After evaporation of the ethereal extract in vacuo, residual precipitate was recrystallized from hexane-ether to give pure 1-allyl-1-hydroxy-2-oxacenaphthene (**16,** 206 mg, 91%), colorless needles: mp 147–148 °C; NMR ($CDCl_3$) δ 2.74 (t, 2 H, CH_2), 3.0 (br, 1 H, OH), 5.06 (m, 2 H, C=CH_2), 5.4–5.9 (m, 1 H, CH=C), 7.6–8.2 (m, 6 H, aromatic H); IR (KBr) 3350 (vs, OH), 2855 (s), 1705 (vs, C=O), 1608 (s), 1496 (s), 1345 (s), 1246 (vs), 1185 (vs), 1055 (s), 1020 (s), 995 and 914 (s, CH=CH_2), 776 cm^{-1} (s); MS *m/e* 224 (P, 8%), 182 (base), 155 (5%), 154 (5%).

Anal. ($C_{15}H_{12}O_2$) C, H.

Quinol from the Reaction of Allyltributyltin with Trimethylbenzoquinone (Reaction 2, Table IV). 2a. To the dichloromethane solution (10 mL) of trimethylbenzoquinone (**15,** 1.0 mmol), BF_3·OEt_2 (5.0 mmol) was added under N_2 at −90 °C, followed by quick addition of **2a** (662 mg, 2.0 mmol). The temperature of the reaction mixture was maintained below −85 °C. After 3 min, the reaction mixture was quenched by the addition of aqueous saturated NaCl solution, followed by partitioning with ether. The ethereal solution was worked up in the usual manner and evaporated in vacuo. NMR analysis of the reaction mixture revealed four products: **6** (23%), allyltrimethylhydroquinone (**18,** 8%), 1-allyl-1-hydroxy-2,3,6-trimethylcyclohexa-2,4-dien-4-one (**16,** 53%), and 1-allyl-1-hydroxy-2,3,5-trimethylcyclohexa-2,4-dien-4-one (**17,** 7%). The products were isolated by preparative layer chromatography, developing twice with $CHCl_3$. The R_f 0.75 band contained **6** (80 mg, 42%). The R_f 0.35 band contained **18** (42 mg, 22%). The R_f 0.25 band contained quinol **16** (44 mg, 23%), a colorless oil: NMR ($CDCl_3$) δ 1.76 (s, 3 H, CH_3), 2.00 (m, 6 H, 2 CH_3), 2.51 (d, 2 H, CH_2, J = 7 Hz), 3.4 (br, 1 H, OH), 4.8–5.3 (m, 3 H, CH=C), 5.92 (q, 1 H, ring H, J = 1 Hz); IR (CCl_4) 3400 (s, OH), 2930 (s), 1665 (vs, C=O), 1620 (vs), 1490 (s), 1480 (s), 1445 (s), 1330 (s), 1045 (s), 1020 (s), 990 (s), 920 (s), 910 (s), 880 cm^{-1} (s); MS *m/e* 192 (P, 40%), 152 (base), 121 (40%), 119 (67%), 117 (66%).

The R_f 0.15 band contained quinol **17** (9 mg, 5%), a colorless oil: NMR ($CDCl_3$) δ 1.83 (m, 6 H, 2 CH_3), 1.96 (s, 3 H, CH_3), 2.47 (d, 2 H, CH_2, J = 7 Hz), 4.8–5.5 (m, 3 H, CH=CH), 6.5 (q, 1 H, ring H, J = 1 Hz); IR (CCl_4) 3440 (s, OH), 2920 (s), 1670 (s, C=O), 1615 (vs), 1440 (s), 1380 (vs), 1025 (s), 990 and 915 (s, CH=CH), 905 cm^{-1} (s); MS *m/e* 192 (P, 3%), 153 (18%), 152 (base).

2b. The reaction was performed according to the same procedure as for **2a,** and after stirring for 5 min at −90 to −85 °C the reaction mixture was quenched. NMR analysis of this reaction mixture revealed four products: **6** (41%), **16** (41%), **17** (7%), and **8** (10%).

2c. The reaction was performed according to the same procedure as for **2a.** After stirring for 20 min at −90 to −85 °C, the reaction mixture was quenched. NMR analysis of this reaction mixture revealed four products: **6** (41%), **16** (41%), **17** (6%), and **18** (10%).

2d. The reaction was performed according to the same procedure as for **2a.** After keeping at −90 to −85 °C for 20 min, the reaction mixture was allowed slowly to warm to −10 °C for 1 h and worked up in the usual manner. NMR analysis of this reaction mixture revealed four products: **6** (55%), **16** (23%), **18** (17%), and **19** (5%).

Rearrangement of Pure Quinols (Table V). Rearrangement products were identified by comparison of their NMR spectra with those of authentic materials.

A. Thermal Rearrangement of 16. Quinol **16** (35 mg, 0.175 mmol) was dissolved in 1 mL of CH_2Cl_2. The solution was refluxed for 8 h and evaporated under reduced pressure. NMR analysis indicated the presence of **18** (80%) and **19** (5%).

B. Protic Acid Catalyzed Rearrangement of 16. Quinol **16** (38.6 mg, 0.196 mmol) was dissolved in 1 mL of CH_2Cl_2 and 0.5 mL of 2 N HCl was added. The mixture was stirred at 20 °C for 2 h. NMR analysis indicated the presence of **6** (11%), **18** (33%), and **16** (55%). The reaction was continued for an additional 4 h. NMR analysis showed the presence of **6** (34%) and **18** (60%).

C. BF_3-Catalyzed Rearrangement of 16. Quinol **16** (23 mg, 0.120 mmol) was dissolved in 1 mL of CH_2Cl_2, and BF_3·OEt_2 (0.21 mmol) was added at −70 °C. Then the reaction mixture was allowed to warm to 20 °C under constant stirring, saturated aqueous NaCl was added, and the mixture was partitioned with eher. After evaporation of organic solvent, NMR analysis indicated **6** (45%) and **18** (55%).

D. Thermal Rearrangement of 17. Quinol **17** (15 mg, 0.078 mmol) was refluxed in 5 mL of CH_2Cl_2 for 5 h. After evaporation of the solvent, NMR analysis showed the sole product to be **6** (100%).

E. Protic Acid Catalyzed Rearrangement of 17. Quinol **17** (15 mg, 0.078 mmol) was dissolved in 1 mL of CH_2Cl_2, and 2 N HCl (0.5 mL) was added at 20 °C. The reaction mixture was stirred for 4 h at 20 °C. After the usual workup, NMR analysis indicated the major product to be **6** (90%), accompanied by a trace amount of **18.**

F. BF_3-Catalyzed Rearrangement of 17. Quinol **17** (6.1 mg, 0.032 mmol) was dissolved in 1.0 mL of CH_2Cl_2 and BF_3OEt_2 (0.04 mmol) was added at −73 °C. After the reaction mixture was allowed to warm to 25 °C, the usual workup gave **6** (47%), **18** (44%), and **7** (9%) by NMR.

Reaction of Allyltributyltin with Trimethylbenzoquinone. Effects

of the Added Amount of BF_3·OEt_2 (Table IV). All the reactions were performed in 1-mmol scale under the standard conditions.

A. The reaction was performed in the presence of 1 equiv (based on the amount of the quinone) of BF_3·OEt_2. NMR analysis indicated the presence of two compounds: **6** (54%) and **8** (30%).

B. The reaction was performed in the presence of 2 equiv of BF_3·OEt_2. NMR analysis indicated the presence of two compounds: **6** (55%) and **8** (41%).

C. The reaction was performed in the presence of 3 equiv of BF_3·OEt_2. NMR analysis indicated the presence of two products: **6** (38%) and **18** (61%).

D. The reaction was performed in the presence of 3 equiv of BF_3·OEt_2. NMR analysis indicated the presence of two products: **6** (21%) and **18** (79%).

Reaction of (2-Methyl-2-propenyl)tributyltin with 2,5-Dimethylbenzoquinone (Reaction 3c). The tin reagent **2b** (690 mg, 2.0 mmol) was added to a CH_2Cl_2 solution (10 mL) of 2,5-dimethylbenzoquinone (136 mg, 1.0 mmol) and BF_3·OEt_2 (0.5 mmol) at −78 °C; then the reaction mixture was allowed to gradually warm up to room temperature. An amount (10 mL) of aqueous saturated NaCl solution was added to the reaction mixture, following the usual workup. NMR analysis indicated the presence of two products: **5** (45%) and **22** (43%).

Reaction of (2-Methyl-2-propenyl)tributyltin with 2,5-Dimethylbenzoquinone (Reaction 3d). The reaction was performed according to the above method using 1.0 mmol of BF_3·OEt_2. NMR analysis indicated the presence of **22** (99.5%). TLC analysis indicated the presence of a trace amount of **5**.

Reaction of 2-Butenyltributyltin with 2-Methoxy-1,4-naphthoquinone. The tin reagent **2c** (690 mg, 2.0 mmol) was added to a CH_2Cl_2 solution of 2-methoxy-1,4-naphthoquinone (**23**) and BF_3·OEt_2 (2.0 mmol) at −78 °C. The reaction mixture was allowed to warm to −30 °C and then quenched with aqueous saturated NaCl solution, following the usual workup. After concentration, the products were separated by preparative layer chromatography, developing twice with CH_2Cl_2. The R_f 0.54 band contained 40 mg (21%) of the starting quinone. The R_f 0.46–0.15 band contained three quinols (in a total yield of 138 mg, 57%). The quinol mixture was separated by medium-pressure liquid chromatography (silica gel column, developing with CH_2Cl_2). The first fraction contained 40 mg (17%) of one diastereomer of 2,3-benzo-1-hydroxy-1-(1-methyl-2-propenyl)-5-methoxycyclohexa-2,5-dien-4-one (**24**), colorless crystals (from CH_2Cl_2–hexane): mp 104–105 °C; NMR ($CDCl_3$) δ 0.77 (d, 3 H, J = 7 Hz), 2.71 (m, 1 H, CH), 3.39 (br, 1 H, OH), 3.83 (s, 3 H, CH_3O), 5.05–5.30 (m, 2 H, C=CH_2), 5.43–5.70 (m, 1 H, CH=C), 5.78 (s, 1 H, ring H), 7.3–7.8 (m, 3 H, aromatic H), 8.10 (m, 1 H, aromatic H); IR (KBr) 3370 (vs, OH), 3090 (m), 2980 (m), 1620 (vs, C=O), 1590 (vs), 1567 (vs), 1450 (s), 1360 (vs), 1230 (vs), 1205 (s), 1190 (vs), 1010 (vs), 993 (s), 953 (vs), 842 (vs), 913 (vs), 785 cm^{-1} (vs).

Anal. ($C_{15}H_{16}O_3$) C, H.

The second fraction contained 17 mg (7%) of another diastereomer (**25**), colorless rhombics (from CH_2Cl_2–hexane): mp 149–150 °C; NMR ($CDCl_3$) δ 0.81 (d, 3 H, CH_3, J = 7 Hz), 2.77 (m, 1 H, CH), 3.09 (s, 1 H, OH), 3.88 (s, 3 H, CH_3O), 4.52–4.88 (m, 2 H, C=CH_2), 5.24–5.64 (m, 1 H, CH=C), 5.80 (s, 1 H, ring H), 7.00–7.48 (m, 3 H, aromatic H), 7.82 (d, 1 H, aromatic H).

Anal. ($C_{15}H_{16}O_3$) C, H.

The third fraction contained a mixture (21 mg, 9%) of two stereoisomers (trans:cis = 80:20) of 2,3-benzo-1-(2-butenyl)-1-hydroxy-6-methoxycyclohexa-2,5-dien-4-one (**26**), colorless rhombics: mp 137–139 °C; NMR ($CDCl_3$) δ 1.34 (d, *trans*-CH_3, J = 7 Hz), 1.46 (d, *cis*-CH_3, J = 7 Hz), 2.82 (m, 2 H, CH_2), 3.42 (br, OH), 3.80 (s, CH_3O), 4.73 (m, CH_2CH=CH), 5.37 (m, C=$CHCH_3$), 5.62 (s, ring H), 7.28–7.80 (m, 3 H, aromatic H), 7.99 (d, aromatic H); IR (KBr) 3380 (vs, OH), 1630 (vs, C=O), 1610 (vs), 1595 (vs), 1570 (vs), 1460 (s), 1364 (s), 1340 (s), 1245 (vs), 1230 (vs), 1020 (vs), 965 (s), 864 (s), 784 (vs), 735 cm^{-1} (s).

Anal. ($C_{15}H_{10}O_3$) C, H.

Reaction of (3-Methyl-2-butenyl)tributyltin with 2-Methoxy-1,4-naphthoquinone. The tin reagent **2e** (718 mg, 2.0 mmol) was added to a CH_2Cl_2 solution (20 mL) of 2-methoxy-1,4-naphthoquinone (**23**, 188 mg, 1.0 mmol) and BF_3·OEt_2 (2.0 mmol) at −78 °C. The reaction mixture was allowed to warm to −50 °C and then quenched with aqueous saturated NaCl solution, following the usual workup. The products were separated by preparative layer chromatography, developing with $CHCl_3$. The R_f 0.82 band contained 32 mg (10%) of 2-(3-methyl-2-butenyl)-3-methoxy-1,4-naphthoquinone (**28**), a yellow oil: NMR ($CDCl_3$) δ 1.69 (s, 3 H, *cis*-CH_3), 1.70 (s, 3 H, *trans*-CH_3), 3.33 (d, 2 H, CH_2, J = 8 Hz), 4.16 (s, 3 H, CH_3O), 5.19 (t, 1 H, CH=C, J = 8 Hz), 7.8–7.9 (m, 2 H, aromatic H), 8.0–8.2 (m, 2 H, aromatic H); IR (CCl_4) 2920 (m), 1670 (vs, C=O), 1650 (s), 1595 (s), 1336 (vs), 1262 (vs), 1240 (s), 1217 (s), 1063 (s), 915 cm^{-1} (s); MS m/e 256 (P, base), 241 (80%), 213 (98%).

Anal. ($C_{16}H_{16}O_3$) C, H.

The R_f 0.33 band contained 38 mg (20%) of the starting quinone. The R_f 0.08 band contained 20 mg (7%) of 2,3-benzo-1-hydroxy-(3-methyl-2-butenyl)-6-methoxycyclohexa-2,4-dien-4-one (**27**), colorless crystals: mp 131–132 °C; NMR ($CDCl_3$) δ 1.30 (s, 3 H, CH_3), 1.48 (s, 3 H, CH_3), 2.73 (t, 2 H, CH_2, J = 8 Hz), 3.0 (br, 1 H, OH), 3.80 (s, 3 H, CH_3O), 4.49 (t, 1 H, CH=C, J = 8 Hz), 5.65 (s, 1 H, ring H), 7.2–7.8 (m, 3 H, ring H), 8.00 (m, 1 H, ring H); IR (KBr) 3370 (vs, OH), 2910 (m), 1620 (vs, C=O), 1600 (vs), 1590 (vs), 1565 (vs), 1450 (s), 1360 (vs), 1230 (vs), 1195 (s), 1060 (s), 1045 (s), 1010 (s), 860 (s), 780 cm^{-1} (s); MS m/e 258.126 ± 0.005 (calcd for $C_{16}H_{18}O_3$, 258.1255).

Reaction of *trans*-2-Butenyltrialkyltin with Quinones. A. With *p*-Benzoquinone. *trans*-2-Butenyltributyltin (**2c**, 690 mg, 2.0 mmol) was added to *p*-benzoquinone (108 mg) and BF_3·OEt_2 (1.0 mmol) in 10 mL of CH_2Cl_2, following the general procedure. After oxidation with aqueous $FeCl_3$ solution, the NMR spectrum of this product showed it to be composed of two types of allylic isomers, 2-butenylbenzoquinone (α adduct, 5%) and (1-methyl-2-propenyl)benzoquinone (γ adduct, 95%). The products were isolated by preparative layer chromatography, developing with 85:15 hexane–ether. The isomeric mixture was obtained (121 mg, 75%), a brown oil: NMR (CCl_4) δ 1.16 (d, CH_3 of γ adduct, J = 7 Hz), 1.72 (d, CH_3 of α adduct, J = 6 Hz), 3.08 (d, CH_2 of α adduct, J = 7 Hz), 3.63 (m, CH of γ adduct), 5.12 (d, CH=CH_2 of γ adduct, J = 12 Hz), 5.14 (d, CH=CH_2 of γ adduct, J = 16 Hz), 5.50 (m, CH=CH of α adduct), 5.8–6.0 (m, CH=CH_2 of γ adduct), 6.50 (s, ring H), 6.74 (s, ring H); IR (neat) 2960 (s), 1660 (vs, C=O), 1600 (vs), 1455 (s), 1354 (s), 1300 (vs), 1013 and 910 (vs, CH=CH_2), 828 cm^{-1} (s); MS m/e 162 (P, 62%), 147 (base), 134 (62%), 119 (65%), 105 (33%), 91 (69%).

Anal. ($C_{10}H_{10}O_2$) C, H.

B. With 2,3-Dimethylbenzoquinone. *trans*-2-Butenyltrimethyltin (**2d**, 525 mg, 2.4 mmol) was added to 2,3-dimethylbenzoquinone (272 mg, 2.0 mmol) and BF_3·OEt_2 (2.0 mmol) in 20 mL of CH_2Cl_2, following the general reaction procedure. After evaporation of the organic solvent, in the residue no α adduct was detected by NMR. Two products were isolated by preparative layer chromatography, developing with 85:15 hexane–ether. The upper band contained the starting quinone (81 mg, 30%). The lower band contained 2,3-dimethyl-5-(3-methyl-2-propenyl)hydroquinone (158 mg, 41%), colorless crystals: mp 74–76 °C; NMR ($CDCl_3$) δ 1.35 (d, 3 H, CH_3, J = 8 Hz), 2.16 (s, 6 H, 2 CH_3), 3.55 (m, 1 H, CH_3CH), 4.44 (s, 1 H, OH), 4.68 (s, 1 H, OH), 5.0–5.3 (m, 2 H, C=CH_2), 5.8–6.2 (m, 1 H, CH=C), 6.42 (s, 1 H, aromatic H); IR (KBr) 3260 (vs, OH), 1630 (m, C=C), 1590 (m), 1410 (vs), 1210 (vs), 1075 (vs), 990 and 910 (s, CH=CH_2), 865 (m), 815 cm^{-1} (m).

Anal. ($C_{12}H_{16}O_2$) C, H.

C. With 2,3-Dichlorobenzoquinone. The tin reagent **2d** (262 mg, 1.2 mmol) was added to 2,3-dichlorobenzoquinone (177 mg, 1.0 mmol) and BF_3·OEt_2 (1.0 mmol) in 10 mL of CH_2Cl_2, following the general reaction procedure. After evaporation of organic solvent in vacuo, NMR analysis of the residue showed it to be two types of allylic isomers, 5-(2-butenyl)-2,3-dichlorohydroquinone (α adduct, 37%) and 2,3-dichloro-5-(1-methyl-2-propenyl)hydroquinone (γ adduct, 63%). This isomeric mixture (205 mg, 88%) was recrystallized from hexane–ether as white needles: mp 92–95 °C; NMR ($CDCl_3$) δ 1.31 (d, CH_3 of γ adduct, J = 8 Hz), 1.68 (m, *cis*- and *trans*-CH_3 of α adduct), 3.31 (m, CH_2 of α adduct), 3.84 (m, CH of γ adduct), 5.02 and 5.15 (m, CH=CH_2 of γ adduct), 5.3 (br, OH), 5.55 (m, CH=CH of α adduct), 5.8–6.2 (m, CH=CH_2 of γ adduct), 6.82 (s, aromatic H); IR (KBr) 3320 (vs, OH), 1490 (s), 1420 (vs), 1400 (vs), 1340 (s), 1300 (s), 1270 (s), 1170 (vs), 1140 (vs), 965 (vs, *trans*-CH=CH), 850 cm^{-1} (vs).

Anal. ($C_{10}H_{10}O_2Cl_2$) C, H, Cl.

D. With 1,4-Naphthoquinone. The tin reagent **2d** (549 mg, 2.5 mmol) was added to 1,4-naphthoquinone (316 mg, 2.0 mmol) and BF_3·OEt_2 (4.0 mmol) in 20 mL of CH_2Cl_2, following the usual reaction procedure. After oxidation with Ag_2O and then evaporation

of the solvent, in the residue no α adduct was detected by NMR. The product was isolated by preparative layer chromatography, developing with 85:15 hexane–ether. The product was isolated and assigned to be 2-(1-methyl-2-propenyl)-1,4-naphthoquinone (364 mg, 98%), a yellow oil: NMR ($CDCl_3$) δ 1.32 (d, 3 H, CH_3, J = 8 Hz), 3.85 (m, 1 H, CH, J = 6, 8 Hz), 5.18 (m, 2 H, CH=CH_2), 5.7–6.1 (m, 1 H, CH=CH_2), 6.76 (s, 1 H, ring H), 7.6–7.8 (m, 2 H, aromatic H), 7.9–8.1 (m, 2 H, aromatic H); IR (neat) 2970 (s), 1655 (vs, C=O), 1590 (s), 1325 (vs), 1300 (vs), 1240 (s), 990 and 915 (s, CH=CH_2), 770 cm^{-1} (s); MS *m/e* 212 (P, 81%), 197 (base).

Anal. ($C_{14}H_{12}O_2$) C, H.

E. With 2,5-Dimethylbenzoquinone. The tin reagent **2c** (864 mg, 2.5 mmol) was added to 2,5-dimethylbenzoquinone (272 mg, 2.0 mmol) and BF_3·OEt_2 (2.0 mmol) in 15 mL of CH_2Cl_2, following the general procedure. After evaporation of the solvent, recrystallization of the residue from $CHCl_3$ gave 3-(2-butenyl)-2,5-dimethylhydroquinone (227 mg, 69%), white needles: mp 153.0–154.5 °C; NMR ($CDCl_3$) δ 1.71 (m, 3 H, *cis*- and *trans*-CH_3), 2.21 (s, 6 H, ring CH_3), 3.40 (br, 2 H, CH_2), 4.6 (br, 2 H, OH), 5.57 (m, 2 H, CH=CH), 6.51 (s, 1 H, aromatic H); IR (KBr) 3300 (vs, OH), 2920 (s), 1627 (w, C=C), 1450 (s), 1385 (s), 1354 (vs), 1220 (vs), 1190 (vs), 1106 (s), 1081 (s), 972 (s), 955 cm^{-1} (s, *trans*-CH=CH); MS *m/e* 192 (P, base), 177 (71%), 175 (18%), 163 (16%), 150 (24%).

After oxidation of the hydroquinone with Ag_2O, the product was separated by preparative layer chromatography, developing with 85:15 hexane–ether. The R_f 0.51 band contained 3-(2-butenyl)-2,5-dimethylbenzoquinone. The NMR spectrum of this quinone showed it to be composed predominantly of a trans isomer of the side chain (trans:cis >98:2), and not to contain a regioisomer (<1%): NMR (CCl_4) δ 1.65 (d, 3 H, CH_3, J = 5 Hz), 2.00 (s, 3 H, ring CH_3), 2.03 (d, 3 H, ring CH_3, J = 1.5 Hz), 3.15 (d, 2 H, CH_2, J = 6 Hz), 5.40 (m, 2 H, CH=CH), 6.54 (q, 1 H, ring H, J = 1.5 Hz); IR (neat) 2930 (m), 1653 (vs, C=O), 1618 (s), 1440 (m), 1380 (m), 1318 (s), 1260 (m), 1187 (m), 962 (s), 883 cm^{-1} (m); MS *m/e* 190 (P, 54%), 175 (base), 162 (22%), 147 (45%).

Anal. ($C_{12}H_{14}O_2$) C, H.

F. With 2,6-Dimethylbenzoquinone. The tin reagent **2c** (1.03 g, 3.0 mmol) was added to 2,6-dimethylbenzoquinone (272 mg, 2.0 mmol) and BF_3·OEt_2 (2.0 mmol) in 15 mL of CH_2Cl_2, following the general procedure. After oxidation with Ag_2O, the products were separated by preparative layer chromatography, developing twice with 95:5 hexane–ether. The upper band contained 44 mg (9%) of 2,6-di(2-butenyl)-3,5-dimethylbenzoquinone, a yellow oil: NMR (CCl_4) δ 1.62 (d, 6 H, 2 CH_3, J = 5 Hz), 1.97 (s, 6 H, 2 CH_3), 3.10 (d, 4 H, CH_2, J = 5 Hz), 5.32 (m, 4 H, CH=CH); IR (neat) 2925 (m), 1645 (vs, C=O), 1438 (m), 1290 (s), 1252 (m), 1204 (m), 964 cm^{-1} (s, *trans*-CH=CH); MS *m/e* 244 (P, 98%), 229 (base), 215 (24%), 201 (19%), 189 (30%), 174 (28%), 159 (48%).

Anal. ($C_{16}H_{20}O_2$) C, H.

The middle band contained 95 mg (25%) of 2-(2-butenyl)-3,5-dimethylbenzoquinone, a yellow oil. The NMR spectrum showed it to be composed predominantly of the trans isomer of the side chain (trans:cis 96:4) and not to contain the regioisomer: NMR (CCl_4) δ 1.60 (d, *trans*-CH_3, J = 5 Hz), 1.72 (d, *cis*-CH_3, J = 6 Hz), 1.99 (s, 2 CH_3), 3.08 (d, *trans*-CH_2, J = 5 Hz), 3.17 (d, *cis*-CH_2, J = 6 Hz), 5.24 (m, CH=CH), 6.36 (s, ring H); IR (neat) 2930 (s), 1648 (vs, C=O), 1617 (s), 1380 (s), 1028 (m), 964 (s, *trans*-CH=CH), 885 cm^{-1} (m); MS *m/e* 190 (P, 57%), 175 (base), 161 (31%), 147 (53%), 119 (21%).

Anal. ($C_{12}H_{14}O_2$) C, H.

The lower band contained 2,6-dimethylbenzoquinone (68 mg, 25%).

G. With 2,5-Di-*tert*-butylbenzoquinone. The tin reagent **2d** (690 mg, 2.0 mmol) was added to 2,5-di-*tert*-butylbenzoquinone (220 mg, 1.0 mmol) and BF_3·OEt_2 (1.0 mmol) in 10 mL of CH_2Cl_2, following the general procedure. The products were isolated by preparative layer chromatography, developing with 1:1 hexane–ether. The upper band contained 2-(2-butenyl)-5-*tert*-butylhydroquinone, white needles, mp 112–113 °C. The regioisomer was not detected by NMR: NMR ($CDCl_3$) δ 1.38 (s, 9 H, $(CH_3)_3$), 1.70 (m, 3 H, CH_3), 3.22 (br, 2 H, CH_2), 4.57 (s, 1 H, OH), 4.58 (s, 1 H, OH) 5.6 (m, 2 H, CH=CH), 6.42 (s, 1 H, ring H), 6.76 (s, 1 H, ring H); IR (KBr) 3300 (vs, OH), 2965 (s), 1417 (vs), 1244 (w), 1190 (vs), 1138 (s), 968 (m, *trans*-CH=CH), 870 cm^{-1} (m); MS *m/e* 220 (P, 37%), 214 (24%), 205 (53%), 203 (42%), 175 (32%), 164 (base), 148 (58%).

Anal. ($C_{14}H_{20}O_2$) C, H.

The lower layer contained 2,5-di-*tert*-butylhydroquinone (164 mg, 56%).

The above allylated hydroquinone easily underwent air oxidation to give the corresponding quinone, of which the stereochemistry of the side chain was determined to be trans:cis $\simeq$ 70:30 by NMR: NMR ($CDCl_4$) δ 1.30 (s, $(CH_3)_3$), 1.68 (d, *cis*-CH_3, J = 4 Hz), 1.74 (d, *trans*-CH_3, J = 4 Hz), 3.06 (m, CH_2), 5.60 (m, CH=CH), 6.38 (t, ring H, J = 1 Hz), 6.49 (s, ring H); IR (neat) 2960 (vs), 1645 (vs, C=O), 1595 (s), 1365 (s), 1250 (s), 1100 (s), 970 (s), 910 cm^{-1}; MS *m/e* 218 (P, 60%), 203 (base), 175 (85%), 162 (36%), 161 (33%), 147 (32%).

Anal. ($C_{14}H_{18}O_2$), C, H.

Acknowledgment. The author is grateful to Professor K. Maruyama for valuable discussions and his continuous encouragement. This research was supported by a grant-in-aid for scientific research from the Ministry of Education (1978–1979).

References and Notes

(1) Synthesis of Naturally Occurring Quinones. 7. A part of this work has been published in a preliminary form (ref 12). Part 6: Naruta, Y.; Maruyama, K. *Chem. Lett.* **1979,** 885.
(2) For a review: Pereyre, M.; Pommer, J.-C. "New Application of Organometallic Reagents in Organic Synthesis", Seyferth, D. Ed.; Elsevier: Amsterdam, 1976; pp 161–218.
(3) (a) Schweig, A.; Weinder, U.; Manuel, G. *J. Organomet. Chem.* **1967,** *54,* 145. (b) Schweig, A.; Weinder, U. *Ibid.* **1967,** *67,* C4. (c) Hanstein, H.; Berwein, H. J.; Trayer, T. G. *J. Am. Chem. Soc.* **1970,** *92,* 7470.
(4) (a) Maruyama, K.; Naruta, Y. *Chem. Lett.* **1978,** 431. (*b*) Naruta, Y.; Ushida, S.; Maruyama, K. *Ibid.* **1979,** 919. (c) Hosomi, A.; Iguchi, H.; Endo, M.; Sakurai, H. *Ibid.* **1979,** 977.
(5) For excellent reviews of quinones and their chemistry see: (a) Morton, R. A., Ed. "Biochemistry of Quinones", Academic Press: New York, 1965. (b) Thomson, R. H. "Naturally Occurring Quinones", 2nd ed.; Academic Press: New York, 1971. (c) Patai, S., Ed. "The Chemistry of the Quinonoid Compounds", Parts 1 and 2; Wiley: New York, 1974.
(6) Fieser, L. F. *J. Am. Chem. Soc.* **1939,** *61,* 2559.
(7) (a) Tishler, M.; Fieser, L. F.; Wender, N. J. *J. Am. Chem. Soc.* **1940,** *62,* 1982. (b) Klose, A. A.; Almquist, H. J. *J. Biol. Chem.* **1940,** *B2,* 462. (c) Hirschmann, R.; Miller, R.; Wendler, N. L. *J. Am. Chem. Soc.* **1954,** *76,* 4592. (d) Isler, O.; Doebel, K. *Helv. Chim. Acta* **1954,** *37,* 225.
(8) Stevens, K. L.; Jurd, L.; Manners, G. *Tetrahedron* **72,** *28,* 1939.
(9) (a) Hegedus, L. S.; Waterman, E. L.; Catlin, J. *J. Am. Chem. Soc.* **1972,** *94,* 7155. (b) Hegedus, L. S.; Evans, B. R. *Ibid.* **1978,** *100,* 3461.
(10) (a) Sato, K.; Inoue, S.; Yamaguchi, R. *J. Org. Chem.* **1972,** *37,* 1889. (b) Sato, K.; Inoue, S.; Saito, K. *J. Chem. Soc., Perkin Trans. 1* **1973,** 2289. (c) Inoue, S.; Yamagami, R.; Sato, K. *Bull. Chem. Soc. Jpn.* **1974,** *47,* 3098. (d) Snyder, C. D.; Rapoport, R. *J. Am. Chem. Soc.* **1974,** *96,* 8046. (e) Evans, D. A.; Hoffman, J. M. *Ibid.* **1976,** *98,* 1983. (f) Raynolds, R. W.; Manning, M. J.; Swenton, J. S. *J. Chem. Soc., Chem. Commun.* **1977,** 499.
(11) Jacobsen, N.; Torssell, K. *Acta Chem. Scand.* **1973,** *27,* 3211.
(12) (a) Maruyama, K.; Naruta, Y. *J. Org. Chem.* **1978,** *43,* 3796. (b) Simple allylation of quinones with allylsilane was also reported: Hosomi, A.; Sakurai, H. *Tetrahedron Lett.* **1977,** 4041.
(13) The strength of Lewis acid–ketone complex was reported in the order $AlCl_3$ > $TiCl_4$ > $SnCl_4$ > BF_3. See: Susz, B. P. *Bull. Soc. Chim. Fr.* **1965,** 2671.
(14) The allylquinol from 2,5-dimethylbenzoquinone is capable of rearranging to allylhydroquinone via [3,3] fashion. However, it would involve eclipsing of a ring methyl group with the side-chain methyl group in the pseudochair transition state; then this pathway may be suppressed (ref 9).
(15) Miller, B. *Acc. Chem. Res.* **1975,** *8,* 245, and references cited therein.
(16) Quinols **25** and **26** are a diastereomeric pair. Their configurations were not determined.
(17) The energy difference between 3-buten-2-yl and 2-buten-1-yl cations is estimated to be 0.3 kcal/mol (at 44.6 °C) based on the hydrolysis of the corresponding chlorides: Vernon, C. A. *J. Chem. Soc.* **1954,** 425, 4462. From the stability of these cations, formation of "γ adduct" might have been expected in every reaction.
(18) Kraus, C. A.; Sessions, W. V. *J. Am. Chem. Soc.* **1925,** *47,* 2361.
(19) Tanaka, J.; Katagiri, T.; Yamada, S. *Nippon Kagaku Zasshi* **1966,** *87,* 877; *Chem. Abstr.* **1966,** *65,* 18449*d*.
(20) Rupe, H.; Bürgin, J. *Chem. Ber.* **1910,** *43,* 172.
(21) Teuber, H.-J.; Rau, W. *Chem. Ber.* **1953,** *86,* 1036.
(22) Fieser, L. F.; Campbell, W. P.; Fry, E. M. *J. Am. Chem. Soc.* **1939,** *61,* 2206.
(23) Otsuki, T. *Bull. Chem. Soc. Jpn.* **1974,** *47,* 3089.
(24) Ullmann, F.; Wenner, P. *Justus Liebigs Ann. Chem.* **1903,** *327,* 116.
(25) Matarasso-Tchiroukhine, E.; Cadiot, P. *J. Organomet. Chem.* **1976,** *121,* 155.
(26) Abel, E. A.; Rowley, R. J. *J. Organomet. Chem.* **1975,** *84,* 199.
(27) Tamborski, C.; Ford, F. E.; Soloski, E. J. *J. Org. Chem.* **1963,** *28,* 237.
(28) Tanigawa, Y.; Moritani, I.; Nishida, S. *J. Organomet. Chem.* **1971,** *28,* 73.
(29) Bohlmann, F.; Kleine, K.-M. *Chem. Ber.* **1966,** *99,* 885.