10a–d was performed under similar conditions as described above and the result was summarized in Table III.

6-Phenyl-6-(phenylthio)hex-5-enal (6a): IR (neat) 1730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.42–2.87 (m, 6 H), 5.93 (t, J = 7.0 Hz, 0.75 H), 6.33 (t, J = 7.0 Hz, 0.25 H), (E/Z = 75:25) 6.82–7.65 (m, 10 H), 9.45–9.78 (m, 1 H); MS, m/e 282 (M^+). Anal. Calcd for $C_{18}H_{18}OS$: C, 76.56; H, 6.42. Found: C, 76.38; H, 6.32.

7-Phenyl-7-(phenylthio)hept-6-en-2-one (6b): IR (neat) 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.08–2.61 (m, 9 H), 6.30 (t, J = 7.0 Hz, 0.67 H), 6.78 (t, J = 5.0 Hz, 0.33 H) (E/Z = 67:33), 6.42–7.72 (m, 10 H); MS, m/e 296 (M^+). Anal. Calcd for $C_{19}H_{20}OS$: C, 76.99; H, 6.80. Found: C, 76.54; H, 6.77.

8-Phenyl-8-(phenylthio)oct-7-enal (6d): IR (neat) 1730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.12–1.92 (m, 6 H), 1.92–2.78 (m, 4 H), 6.05 (t, J = 7.5 Hz, 0.6 H), 6.35 (t, J = 7.5 Hz, 0.4 H) (E/Z = 60:40), 6.92–7.40 (m, 10 H), 9.55–9.75 (m, 1 H); MS, m/e 310 (M^+). Anal. Calcd for $C_{20}H_{22}OS$; C, 77.38; H, 7.14. Found: C, 77.38; H, 7.13.

9-Phenyl-9-(phenylthio)non-8-en-2-one (6e): IR (neat) 1715 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.86–2.73 (m, 13 H), 6.06 (t, J = 7.0 Hz, 0.6 H), 6.36 (t, J = 7.0 Hz, 0.4 H) (E/Z = 60:40), 6.73–7.66 (m, 10 H); MS, m/e 324 (M^+). Anal. Calcd for $C_{21}H_{24}OS$: C, 77.73; H, 7.45. Found: C, 77.70; H, 7.42.

8-Phenyl-8-(phenylthio)oct-7-en-2-one (6g): IR (neat) 1715 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.27–2.80 (m, 11 H), 6.03 (t, J = 7.0 Hz, 0.25 H), 6.35 (t, J = 7.0 Hz, 0.75 H) (E/Z = 25:75), 7.00–7.42 (m, 10 H), MS, m/e 310 (M^+). Anal. Calcd for $C_{20}H_{22}OS$: C, 77.38; H, 7.14. Found: C, 77.17; H, 7.11.

Ring-Opening Reaction of *trans*-2-[Bis(phenylthio)-methyl]cyclohexanol (14). Cyclohexanol 14 was treated with NCS and triethylamine under typical conditions as described above and the reaction mixture was separated by MPLC using benzene to give 7,7-bis(phenylthio)hept-6-enal (**15**) (14%)[20] and 6,7-bis(phenylthio)-7-chloroheptanol (**16**) (14%). **15**: IR (neat) 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.35–1.81 (m, 4 H), 2.20–2.64 (m, 4 H), 6.23 (t, J = 7.4 Hz, 1 H), 7.04–7.40 (m, 10 H), 9.62 (t, J = 1.5 Hz, 1 H); MS, m/e 328 (M^+). Anal. Calcd for $C_{19}H_{20}OS_2$: C, 69.47; H, 6.14. Found: C, 69.29; H, 6.05. This compound was identified with an authentic sample prepared by the reaction of 5-(ethoxycarbonyl)valeraldehyde with [bis(phenylthio)(trimethylsilyl)methyl]lithium, followed by reduction (LAH) and oxidation (PPC). **16**: IR (neat) 1730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.50–1.87 (m, 6 H), 2.24–2.67 (m, 2 H), 2.77–3.14 (m, 2 H), 6.87–7.40 (m, 10 H), 9.69 (m, 1 H); MS, m/e 362 (M^+). Anal. Calcd for $C_{19}H_{21}ClOS_2$: C, 62.53; H, 5.80. Found: C, 62.67; H, 6.07.

Reaction of 7-(Phenylthio)hept-6-enal Ethylene Acetal (20) with Phenylsulfenyl Chloride. Phenylsulfenyl chloride (0.29 g, 2.0 mmol) was added to a solution of the ethylene acetal **20** (0.53 g, 2.0 mmol) in dry dichloromethane (20 mL) at −10 °C under nitrogen and stirred for 1 h. The mixture was quenched with water (10 mL), extracted with ether, washed with brine, dried ($MgSO_4$), and concentrated in vacuo. The residue was purified by MPLC using benzene to give 7-oxo-6-(phenylthio)heptanal ethylene acetal (**22**) (0.33 g, 60%); IR (neat) 1730, 1585, 1480, 1442, 1140, 1030 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.27–1.93 (m, 8 H), 3.13–3.73 (m, 1 H), 3.73–4.03 (m, 4 H), 4.16 (t, J = 4.2 Hz, 1 H), 7.13–7.47 (m, 5 H), 9.34 (d, J = 4.1 Hz, 1 H). Anal. Calcd for $C_{15}H_{20}O_3S$: C, 64.26; H, 7.19. Found: C, 64.10; H, 7.01.

8-Methyl-7-(phenylthio)nona-6(*E* or *Z*),8-dienal (24). The *E* and *Z* dienals **24** were prepared from *trans-erythro*-cyclohexanol **23a** and the cis-threo isomer **23b**, respectively, according to the general procedure (*E*, 48%, and *Z*, 44% yields):[20] IR (neat) 3060, 2940, 2860, 1730, 1580, 1480, 1440 cm^{-1}; ^1H NMR ($CDCl_3$) δ (*E* isomer) 1.02–2.58 (m, 8 H), 1.80 (s, 3 H), 4.65–5.02 (m, 2 H), 5.81 (t, J = 1.8 Hz, 1 H), 6.98–7.68 (m, 5 H), 9.60 (t, J = 1.8 Hz, 1 H), (*Z* isomer) 1.03–2.67 (m, 8 H), 1.93 (s, 3 H), 4.80–5.10 (m, 2 H), 6.22 (t, J = 2.0 Hz, 1 H), 7.23–7.68 (m, 5 H), 9.57 (t, J = 2.0 Hz, 1 H); MS, m/e 260 (M^+).

7-(Phenylthio)non-6-en-8-yn-1-al (26): 75% yield by NMR, 25% isolated yield;[20] IR (neat) 3700–3100, 2950, 2870, 1720, 1580, 1480, 1440 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.25–1.95 (m, 4 H), 2.22–2.65 (m, 4 H), 3.12 (s, 1 H), 6.32 (t, J = 7.6 Hz, 1 H), 7.12–7.48 (m, 5 H), 9.72 (t, J = 1.6 Hz, 1 H); MS, m/e 244 (M^+).

7-(Phenylthio)-7-(trimethylsilyl)hept-6-enal (28). A mixture of (*E*)- and (*Z*)-heptenals **28**[20] was obtained in 80% yield, which was separeted into pure isomers (ratio, 80:20) by MPLC using benzene. *E* isomer: IR (neat) 3070, 2950, 1735, 1580, 1480, 1440, 1250, 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.10 (s, 9 H), 1.32–1.85 (m, 4 H), 2.22–2.68 (m, 4 H), 6.54 (t, J = 6.8 Hz, 1 H), 7.17 (br s, 5 H), 9.68 (m, 1 H); MS, m/e 292 (M^+). Anal. Calcd for $C_{16}H_{24}OSSi$: C, 65.92; H, 8.30. Found: C, 65.61; H, 8.28. *Z* isomer: IR (neat) 3070, 2950, 1730, 1580, 1480, 1250, 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.07 (s, 9 H), 1.40–1.90 (m, 4 H), 2.07–2.64 (m, 4 H), 6.09 (t, J = 5.0 Hz, 1 H), 7.27 (br s, 5 H), 9.62 (t, J = 2.0 Hz, 1 H); MS, m/e 292 (M^+). Anal. Calcd for $C_{16}H_{24}OSSi$: C, 65.92; H, 8.30. Found: C, 66.34; H, 8.31. The minor (*Z*)-**28** was gradually isomerized to (*E*)-**28** on standing at room temperature. When the ring-opening reaction was performed by using an excessive amount of NCS (1.5 equiv), 7-(phenylthio)hept-6(*E*)-enal (**29**) was isolated as nearly one stereoisomer in 60% yield: IR (neat) 2940, 1730, 1585, 1480, 1440 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.37–1.77 (m, 4 H), 2.10–2.57 (m, 4 H), 5.60–6.30 (m, 2 H), 7.20 (br s, 5 H), 9.63 (t, J = 2.0 Hz, 1 H). Anal. Calcd for $C_{13}H_{16}OS$: C, 70.87; H, 7.32. Found: C, 70.63; H, 7.20. This heptenal **29** was oxidized to the sulfone (2.6 equiv of MCPBA, CH_2Cl_2, room temperature, 6 h) to determine its stereochemistry by using the coupling constant between the olefinic protons: IR (neat) 1735, 1630, 1320, 1150 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.33–1.97 (m, 4 H), 2.13–2.68 (m, 4 H), 6.31 (dt, J = 15.0 and 1.2 Hz, 1 H), 6.98 (dt, J = 15.0 and 6.6 Hz, 1 H), 7.43–7.70 (m, 3 H), 7.77–8.03 (m, 2 H), 9.70 (t, J = 2.0 Hz, 1 H).

Stereochemistry in the Reactions of (*Z*)- and (*E*)-Allyltributylstannyl Reagents with Quinones

Akio Takuwa,* Osamu Soga, and Taeko Mishima

Department of Chemistry, Faculty of Science, Shimane University, Matsue 690, Japan

Kazuhiro Maruyama

Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606, Japan

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In the BF_3-catalyzed allylation of quinones with allylstanyl reagents, (*Z*)-2-hexenyltributylstannane (**3**) is introduced with no retention of the original double-bond stereochemistry, and neryl reagent (**5**) is introduced with partial loss of olefin stereochemistry. In contrast, (*E*)-2-hexenyltributylstannane (**4**) and geranyltributylstannane (**6**) are introduced with complete retention of their olefin geometries.

The stereochemical fate of an introduced moiety into an aromatic nucleus is of current importance in synthetic organic chemistry. Because of high interest in the synthesis of naturally occurring quinones, the stereoselective introduction of all (*E*)-prenyl functions into the *p*-quinone nucleus has been extensively investigated.[1] Naruta and

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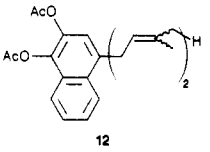
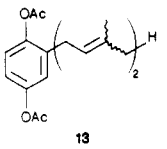
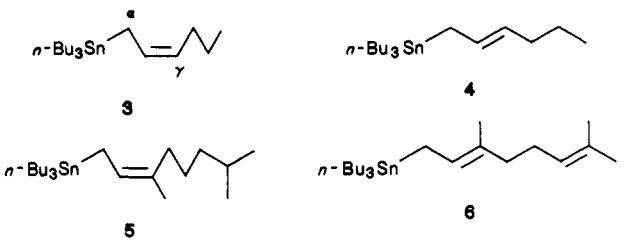
Table I. Reactions of Quinones with Stannyl Reagents (3, 4, 5, and 6)

entry	quinone	stannyl reagent	product	regioisomeric ratio[a] α/γ	stereochemistry at $\Delta^{2'}$ of α-adduct, E/Z[b]	total yield,[c] %
1	1a	3	7a + 8a	78:22	93/7	88
2		4	7a + 8a	71:29	95/5	90
3	1b	3	7b + 8b	50:50	96/4	90
4		4	7b + 8b	36:63	98/2	91
5	1c	3	8c	1:>99		95
6		4	8c	0:100		94
7	1d	3	7d	100:0	75/25	92
8		4	7d	100:0	85/15	93
9		3[d]	7d	100:0	68/32	20
10		4[d]	7d	100:0	69/31	17
11	2a	3	10a	0:100		60
12		4	10a	0:100		55
13	2b	3	9b	100:0	95/5	90[e]
14		4	9b	100:0	>99/1	90[e]
15	2c	4	10c	0:100		50
16	2d	3	9d	100:0	89/11	47
17		4	9d	100:0	91/9	45
18	1a	5	 12	100:0	34/66	60
19		6	12	100:0	95/5	63
20	2a	5	 13	100:0	32/68	51
21		6	13	100:0	96/4	50
22	2d	5	vitamin $K_{2(10)}$	100:0	33/67	20
23		6	vitamin $K_{2(10)}$	100:0	97/3	25

[a] The regioisomeric ratio was determined by ^{1}H NMR spectroscopy and GLPC analysis. [b] The stereochemistry was determined by GLPC analysis and/or ^{1}H NMR spectroscopy. [c] Isolated yield. [d] The reaction was performed in the absence of BF_3·OEt_2. [e] Isolated yield after acetylation.

his co-workers[2] recently developed the direct introduction of a prenyl moiety into a *p*-quinone nucleus by the BF_3·OEt_2-catalyzed-reaction of *p*-quinones with (*E*)-polyprenyltrimethylstannanes, and they successfully synthesized a series of coenzyme Q_n (n = 2–10), vitamin K, vitamin $K_{2(10)}$, and related polyprenylquinones in which a *E* configuration at the $\Delta^{2'}$ position in the products was completely maintained. More recently, we reported that the (*E*)-2-butenyl group was also introduced with retention of the stereochemistry at the Δ^2 position in the BF_3-mediated reaction of *o*-quinones with (*E*)-2-butenyltributylstannane.[3] However, the reaction of quinones with (*Z*)-allylstannyl reagents has been scarcely studied, and the process of introducing a (*Z*)-allyl moiety is still unsolved.

The allylstannyl reagent chosen for the present study is (*Z*)-2-hexenyltributylstannane (**3**), since the lower (*Z*)-alkenyltributylstannane, for example, (*Z*)-2-butenyltributylstannane is unstable and undergoes facile isomerization.[4] For the comparison of the stereochemical fate of the (*Z*)-2-hexenyl moiety with that of the *E* isomer, the reaction of (*E*)-2-hexenyltributylstannane (**4**) with quinones was also examined. Similarly, neryl- (**5**) and geranyltributylstannane (**6**) were used as polyprenylstannyl reagents.



The reaction was performed by treatment of 1 equiv of quinone with 1.2 equiv of allylstannyl reagent in the presence of 3 equiv of BF_3·OEt_2 in dichloromethane under a nitrogen atmosphere at −78 °C as reported previously.[3a,5]

In agreement with the results of (*E*)-2-butenyltributylstannane,[3a] the reaction of **3** and **4** with 1,2-naphthoquinones (**1a–d**) afforded a mixture of α-adduct (**7**) and γ-adduct (**8**), and the regioisomeric ratio (α vs. γ) of the products was strongly affected by the electronic nature of substituent on the quinone nucleus: an electron-donating group resulted in the preferential formation of the α-adduct while an electron-attracting group caused the predominant or exclusive formation of the γ-adduct[3a] (eq 1 and entries 1–8 in Table I).

In the reaction of *p*-quinones with **3** and **4**, more dramatic aspects in the regioselectivity were observed and

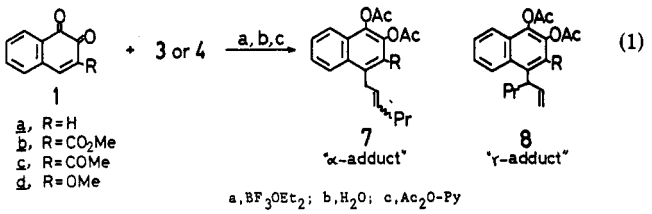
(1) (a) Synder, C. D.; Rapoport, H. *J. Am. Chem. Soc.* **1974**, *96*, 8064. (b) Raynold, R. W.; Manning, M. J.; Swenton, J. S. *J. Chem. Soc., Chem. Commum.* **1977**, 499. (c) Jackman, L. M.; Schudel, P.; Koffer, M.; Isler, O. *Helv. Chim. Acta* **1965**, *48*, 1332. (d) Inoue, S.; Yamagami, R.; Sato, K. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 3098.

(2) (a) Maruyama, K.; Naruta, Y. *J. Org. Chem.* **1978**, *43*, 3796. (b) Naruta, Y.; Maruyama, K. *Chem. Lett.* **1979**, 881, 885. (c) Naruta, Y. *J. Org. Chem.* **1980**, *45*, 4097.

(3) (a) Takuwa, A.; Naruta. Y.; Soga, O.; Maruyama, K. *J. Org. Chem.* **1984**, *49*, 1857. (b) Maruyama, K.; Takuwa, A.; Soga, O. *Nippon Kagaku Kaishi* **1985**, 362.

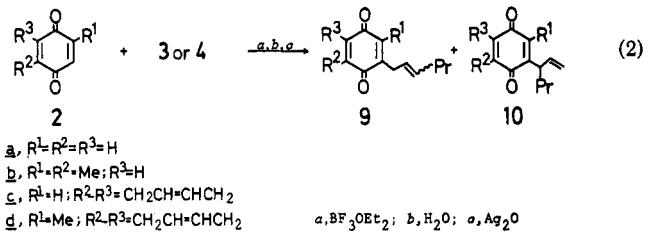
(4) Yatagai, H.; Yamamoto, Y.; Maruyama, K. *J. Am. Chem. Soc.* **1980**, *102*, 4548.

(5) Naruta, Y. *J. Am. Chem. Soc.* **1980**, *102*, 3774.



(1)

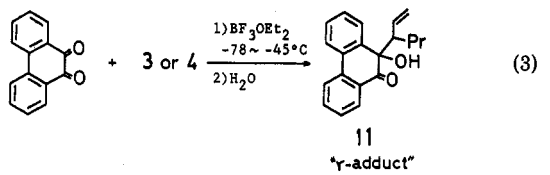
appeared to depend on the bulkiness of the substituent on the quinone nucleus:[5] *p*-benzoquinone (**2a**) and 1,4-naphthoquinone (**2c**) gave γ-adduct **10**, while 2,5-dimethyl-*p*-benzoquinone (**2b**) and 2-methyl-1,4-naphthoquinone (**2d**) exclusively afforded α-adduct **9** (eq 2, entries 11–17 in Table I).



(2)

Turning attention to the stereochemistry at the $\Delta^{2'}$ position of the α-adducts (**7** and **9**), we found that the (*E*)-2-hexenyl group of **4** was introduced with complete retention of the double-bond stereochemistry (entries 2, 4, 8, 14, 17). However, to our surprise, in the reaction of **3** with quinones the (*Z*)-2-hexenyl group was not introduced with stereochemical retention of the original double-bond, but its configuration was almost completely lost to give preferentially or predominantly *E* product at the $\Delta^{2'}$ position (entries 1, 3, 7, 13, 16). In order to avoid the possibility of preisomerization of **3** to **4** by the action of BF_3·OEt_2, the reaction was carried out in the absence of the Lewis acid.[6] Even in such conditions, the *E* product was preferentially obtained from the reaction of 3-methoxy-1,2-naphthoquinone (**1d**) with **3** (entries 9, 10).[6] The result indicates that the lack of stereoselectivity of **3** is not due to the self-isomerization of **3** to **4**, but it should occur during the course of the reaction.

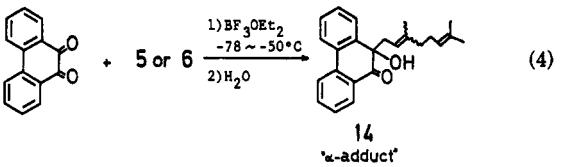
It has been reported[3a,5] that the reaction of an allylstannyl reagents with quinones principally proceeds via 1,2-addition and subsequent allyl migration. To clarify the orientation of the initial 1,2-addition of **3** and **4** to quinones, the reaction of 9,10-phenanthrenequinone with **3** and **4** was examined. When 9,10-phenanthrenenquinone was treated with **3** and **4** respectively in the presence of BF_3·OEt_2, an identical 1,2-addition product (**11**, γ-adduct) was obtained from both reactions (eq 3). Thus the 1,2-



(3)

addition of **3** and **4** quinones occurs at the γ-allyl terminus, and the resulting 1,2-addition products undergoes allyl migration[3a,5] ([3,3]-rearrangement) to afford α-adducts (**7** and **9**).[7] In these processes, the olefin geometry of the (*E*)-2-hexenyl group was maintained, but the olefin geometry of the (*Z*)-2-hexenyl group was converted to the more stable *E* configuration during the course of the reaction. This is the reason for the formation of *E* products ((*E*)-**7** and -**9**) at the $\Delta^{2'}$ position being predominantly formed in the reaction of the quinones with **3**.

We next examined the reactions of **5** and **6** with quinones in the presence of BF_3·OEt_2. In these reactions the α-adduct (**12**, **13**, or vitamin $K_{2(10)}$) was the sole product, in which the geranyl function was introduced with complete retention of the original stereochemistry at the $\Delta^{2'}$ position ($E/Z \sim 96/4$). The neryl group was also introduced with retention of olefin stereochemistry but less stereoselectivity ($E/Z \sim 32/68$) as shown in Table I (entries 18–23).[8] In order to clarify the orientation of these stannyl reagents in the initial 1,2-addition process, we also examined the reaction with 9,10-phenanthrenequinone. When 9,10-phenanthrenequinone was treated with **5** and **6** respectively and quenched at −50 °C, a 1,2-addition product (**14**, α-adduct)[9] was obtained in both cases (eq 4).



(4)

The results indicate that the initial 1,2-addition of these polyprenylstannyl reagents to quinones occurs at the α-allyl terminus, because γ-addition of these reagents suffers from more serious steric interactions.[3a,5] The resulting 1,2-addition intermediates rearranges ([1,3]-rearrangement) to give **12**, **13**, or vitamin $K_{2(10)}$.[10] During these processes the stereochemistry of the geranyl group is completely maintained and that of the neryl group is maintained to some extent.

In conclusion, the differences in stereoselectivity between **3** and **5** might be caused both by the orientation of the allyl moiety in the initial 1,2-addition (α- or γ-addition) and by the mode of rearrangement, which are strongly affected by the steric interaction between the introduced allyl moiety and quinone. Simple steric considerations for the allylstannyl reagents also predict the differences in the stereoselectivity. Reagent **3** has a disubstituted double bond while **5** has trisubstituted double bond. Therefore the *Z* configuration of the 2-hexenyl group could be more easily isomerized to the more stable *E* configuration than that of the neryl group. This is suggested as an additional reason for maintenance of higher stereoselectivity in the stereochemistry of the neryl group compared to the (*Z*)-2-hexenyl group.

Experimental Section

Infrared spectra were measured with a Hitachi 260-50 spectrometer. Nuclear magnetic resonance spectra were measured with a JEOL MH-100 or GX-270 spectrometer with Me_4Si as internal standard. GC–mass spectra were taken with a JEOL 9H-100 spectrometer. GLPC analysis was performed on a Hitachi 613 gas chromatograph equipped with a column of SE-30 (2 m) or Silicon DC-550 (4 m). Dichloromethane was distilled from calcium hydride. Quinones were prepared by the methods described previously.[3a,5]

(6) 1,2-Naphthoquinones react with stannyl reagents such as allyl- or crotyltributylstannane in the absence of BF_3·OEt_2, but in low efficiency; ref 3.

(7) The mechanisms for the formation of γ-adducts, **8** and **10**, are also discussed in previous papers; ref 3a and 5.

(8) Similar stereoselective introduction of geranyl and neryl functions was observed in the reactions of *p*-quinones with geranyl- and neryltrimethylstannanes; ref 2c.

(9) Unfortunately, in spite of several efforts the stereoisomeric ratio of **14** at the $\Delta^{2'}$-position could not be determined.

(10) The similar mode of 1,2-addition and subsequent rearrangement were observed in the reaction of quinones with (3-methyl-2-butenyl)tributylstannane; ref 3a and 5.

(Z)-2-Hexenyltributylstannane (3). This stannyl reagent was prepared by the reaction of (tributylstannyl)lithium[11] with (Z)-2-hexenyl chloride[12] or by the coupling reaction of the boron-stabilized allyl carbanion with tributyltin chloride:[4] bp 145–147 °C (3 mm); NMR (CCl_4) δ 0.90, 1.35 (m, 32 H, 3 C_4H_9 and CH_2CH_3), 1.64 (d, 2 H, CH_2Sn, J = 8 Hz), 1.90 (q, 2 H, C=CCH_2, J = 7 Hz), 4.94 (m, 1 H, C=CHPr), 5.39 (m, 1 H, CH_2CH=C) [The coupling constant (J = 11 Hz) of the olefinic protons determined by spin-decoupling techniques indicates the Z configuration.]; IR ($CHCl_3$) 2950 (vs), 2920 (vs), 1630 (w, C=C), 1460 (s), 1377 (s), 1065 (s), 860 (s) cm^{-1}. The isomeric purity was >97% Z by GLPC analysis.

(E)-2-Hexenyltributylstannane (4). This stannyl reagent was prepared by the reaction of (tributylstannyl)lithium with (E)-2-hexenyl chloride: bp 150–153 °C (2 mm); NMR (CCl_4) δ 0.90, 1.40 (m, 32 H, 3 C_4H_9 and CH_2CH_3), 1.63 (d, 2 H, CH_2Sn, J = 7 Hz), 1.90 (q, 2 H, C=CCH_2, J = 7 Hz), 5.25 (m, 2 H, CH=CH) [The coupling constant (J = 16 Hz) of the olefinic protons determined by spin-decoupling techniques indicates the E configuration.]; IR ($CHCl_3$) 2950 (vs), 2920 (vs), 1645 (w, C=C), 1460 (s), 1375 (s), 1063 (s), 858 (s) cm^{-1}. The isomeric purity was >96% E by GLPC analysis.

Neryltributylstannane (5). This stannyl reagent was prepared by the reaction of (tributylstannyl)lithium with neryl chloride according to Naruta's method:[13] bp 179–182 °C (2 mm); NMR (CCl_4) δ 0.90, 1.36 (m, 27 H, 3 C_4H_9), 1.58, 1.65 (each s, 11 H, 3 CH_3 and CH_2Sn), 1.93 (m, 4 H, CH_2CH_2), 4.96 (m, 1 H), 5.24 (br t, 1 H, J = 7 Hz); IR (CCl_4) 2960 (vs), 2925 (vs), 1460 (s), 1378 (s), 1070 (m) cm^{-1}. The isomeric purity (>97% Z) was determined by GLPC analysis.

Geranyltributylstannane (6). This stannyl reagent was prepared by the reaction of (tributylstannyl)lithium with geranyl chloride according to Naruta's method:[13] bp 177–178 °C (2 mm); NMR (CCl_4) δ 0.83 and 1.36 (m, 27 H), 1.51 (s, 3 H, $\Delta^{2'}$-(E)-CH_3), 1.57, 1.63 (each br s, 8 H, terminal CH_3 and CH_2Sn), 1.94 (m, 4 H), 4.98 (m, 1 H), 5.20 (br t, 1 H, J = 8 Hz); IR (CCl_4) 2955 (vs), 2930 (vs), 1455 (s), 1375 (s), 1063 (m) cm^{-1}. The isomeric purity (96% E) was determined by GLPC analysis.

General Reaction Procedure. To a dichloromethane solution (10 mL) of a quinone (0.5 mmol) was added BF_3·OEt_2 (1.5 mmol) under N_2 at −78 °C. After a few minutes an allylstannyl reagent (0.6 mmol) was added dropwise, and then the temperature of the resulting solution was elevated to 0 °C. The reaction mixture was quenched with 5 mL of saturated aqueous NaCl solution, followed by extraction with CH_2Cl_2. The organic phase was washed with water and dried over Na_2SO_4. After evaporation of the solvent, acetic anhdride–pyridine or Ag_2O was added to the resulting mixture. The product was isolated by preparative layer chromatography, developing with chloroform, benzene, or an ether–hexane mixture. The allyl-substituted products were further purified by preparative TLC or by recrystallization. The isomeric purity and regioisomeric ratio were determined by GLPC and/or NMR analyses, and the results are given in Table I.

Reactions of (Z)- and (E)-2-Hexenyltributylstannane (3 and 4) with Quinones (eq 1 and 2, Table I). A. The reaction of 1,2-naphthoquinone (**1a**) with **3** and **4** was undertaken according to the general procedure. The product was isolated and purified by preparative TLC, developing with chloroform. The R_f 0.65 band contained a mixture of **7a** and **8a**, a pale yellow oil: NMR (CCl_4) δ 0.86 (br t, CH_3, of α and γ, J = 7 Hz), 1.35, 1.93 (each m, CH_2CH_2 of α and γ), 2.18, 2.28 (each s, $OCOCH_3$ of α and γ), 3.97 (d, CH_2 of α, J = 6 Hz), 4.02 (m, CH of γ), 5.05 (m, C=CH_2 of γ), 5.55 (m, CH=CH of α), 5.90 (m, CH=C of γ), 7.10–7.98 (m, Ar H of α and γ); IR (CCl_4) 2955, 2930, 1780, 1368, 1205, 810 cm^{-1}. GC–MS analysis indicated that three isomeric components ((Z)- and (E)-**7a** and **8a**) were contained in the mixture [each M^+ (m/z) 326].

B. The reaction of **1b** with **3** and **4** was carried out according to the general procedure. The product was isolated and purified by preparative TLC, developing twice with chloroform. The R_f 0.60 band contained a mixture of **7b** and **8b**, a pale yellow oil: NMR (CCl_4) δ 0.96 (m, CH_3 of α and γ), 1.28, 1.93 (m, CH_2CH_2 of α and γ), 2.14, 2.26 (each s, $OCOCH_3$ of α and γ), 3.73 (m, $ArCH_2$ of α and CH of γ), 3.83 (s, CO_2CH_3 of α and γ), 5.08 (m, C=CH_2 of γ), 5.55 (m, CH=CH of α), 6.13 (m, CH=C of γ), 7.35–8.25 (m, Ar H of α and γ); IR ($CHCl_3$) 3005, 2950, 2925, 1780, 1725, 1362, 1180, 1020 cm^{-1}.

C. The reaction of **1c** with **3** and **4** was carried out according to the general procedure. After routine isolation and purification by preparative TLC (chloroform, two developments), γ-adduct **8c** was obtained as a yellow oil: NMR (CCl_4) δ 0.82 (t, 3 H, CH_3, J = 7 Hz), 1.20 (m, 2 H, CH_2), 1.93 (br t, 2 H, CH_2, J = 7 Hz), 2.12, 2.26 (each s, 6 H, $OCOCH_3$), 2.38 (s, 3 H, $COCH_3$), 3.61 (m, 1 H, CH), 5.02 (m, 2 H, C=CH_2), 6.22 (m, 1 H, CH=C), 7.30–8.13 (m, 4 H, Ar H); IR ($CHCl_3$) 2950, 2925, 1780, 1723, 1362, 1180 cm^{-1}.

Anal. Calcd for $C_{22}H_{24}O_5$: C, 71.72; H, 6.57. Found: C; 71.49; H, 6.69.

D. The reaction of **1d** with **3** and **4** was carried out according to the general procedure. After routine isolation and purification by preparative TLC (chloroform, three developments), α-adduct **7d** was obtained, a colorless oil: NMR (CCl_4) δ 0.81 (t, CH_3 of E, J = 7 Hz), 0.97 (t, CH_3 of Z, J = 7 Hz), 1.30, 1.90 (each m, CH_2CH_2), 2.18, 2.25 (each s, $OCOCH_3$), 3.67 (m, $ArCH_2$), 3.71 (s, OCH_3), 5.40 (m, CH=CH), 7.19–7.82 (m, Ar H); IR ($CHCl_3$) 2950, 2920, 1775, 1367, 1185, 1172, 1093, 1015 cm^{-1}. GC–MS analysis also showed that the product contained two isomeric components [(E)- and (Z)-**7d**: each M^+ (m/z) 356].

The reaction of **1d** with **3** and **4** in the absence of BF_3·OEt_2 was carried out by the following procedure. To a dichloromethane solution of **1d** (1 equiv) was added the stannyl reagent (1.3 equiv) at −78 °C under a nitrogen atmosphere. The reaction mixture was warmed to 0 °C and quenched with water, followed by extraction with CH_2Cl_2. The combined organic phase was dried and evaporated, and then the resulting oil was treated with acetic anhydride–pyridine. Usual workup gave **7d**.

E. The reaction of **2a** with **3** and **4** was carried out according to the general procedure. The product was isolated and purified by preparative TLC, developing twice with benzene. The R_f 0.43 band contained γ-adduct **10a**, a yellow oil: NMR (CCl_4) δ 0.92 (t, 3 H, CH_3, J = 7 Hz), 1.18–1.63 (m, 4 H, CH_2CH_2), 3.42 (q, 1 H, CH, J = 7 Hz), 5.06 (m, 2 H, C=CH_2), 5.70 (m, 1 H, CH=C), 6.43 (s, 1 H, quinonoid H), 6.66 (s, 2 H, quinonoid H); IR ($CHCl_3$) 2952, 2930, 1662, 1300, 920 cm^{-1}.

F. The reaction of **2b** with **3** and **4** was carried out according to the general procedure. After acetylation with acetic anhydride–pyridine, the product was isolated and purified by preparative TLC, developing twice with chloroform. The R_f 0.80 band contained 2,5-dimethyl-3-(2-hexenyl)benzene-1,4-diyl diacetate, a colorless oil: NMR (CCl_4) δ 0.85 (t, 3 H, CH_3, J = 7 Hz), 1.31, 1.93 (each m, 4 H, CH_2CH_2), 1.97 (s, 3 H, ring CH_3), 2.02 (s, 3 H, ring CH_3), 2.15 (s, 6 H, $OCOCH_3$), 3.13 (br s, 2 H, CH_2), 5.22 (m, 2 H, CH=CH), 6.60 (s, 1 H, Ar H); IR ($CHCl_3$) 2950, 2920, 1760, 1375, 1180 cm^{-1}.

Anal. Calcd for $C_{18}H_{24}O_4$: C, 71.03; H, 7.95. Found: C, 70.81; H, 7.89.

G. The reaction of **2c** with **4** was carried out according to the general procedure. The product was isolated and purified by preparative TLC, developing twice with benzene. The R_f 0.62 band contained γ-adduct **10c**, a yellow oil: NMR (CCl_4) δ 0.95 (t, 3 H, CH_3, J = 7 Hz), 1.25–1.77 (m, 4 H, CH_2CH_2), 3.72 (q, 1 H, CH, J = 7.5 Hz), 5.20 (m, 2 H, C=CH_2), 5.90 (m, 1 H, CH=C), 6.75 (s, 1 H, quinonoid H), 7.70–8.18 (m, 4 H, Ar H); IR ($CHCl_3$) 2950, 2920, 1660, 1610, 1595, 1325, 1302, 1260 cm^{-1}.

H. The reaction of **2d** with **3** and **4** was carried out according to the general procedure. The product was isolated and purified by preparative TLC, developing twice with 3:2 ether/hexane. The R_f 0.82 band contained α-adduct **9d**, a yellow oil: NMR (CCl_4) δ 0.86 and 0.96 (each t, 3 H, trans and cis side chain CH_3, J = 7 Hz), 1.35, 1.95 (each m, 4 H, CH_2CH_2), 2.15 (s, 3 H, ring CH_3), 3.30 (d, 2 H, CH_2, J = 6 Hz), 5.45 (m, 2 H, CH=CH), 7.62–8.10 (m, 4 H, Ar H); IR (CCl_4) 2950, 2920, 1660, 1290 cm^{-1}. GC–MS analysis showed that the product contained two isomeric com-

(11) Tamborski, C.; Ford, F. E.; Soloski, E. J. *J. Org. Chem.* **1963**, *28*, 237.

(12) Stannylation of 2-butenyl chloride with stannyllithium has been reported to proceed with retention of the stereochemistry at the Δ^2-position. Matarasso-Tchiroukhine, E.; Cadiot, P. *J. Organomet. Chem.* **1976**, *121*, 155.

(13) These coupling reactions proceed via an S_N2 mechanism with perfect retention of the Δ^2 stereochemistry of the polyprenyl halides; ref 2c.

ponents [(*E*)- and (*Z*)-**9d**: each M^+ (*m/z*) 254].

Reactions of 3 and 4 with 9,10-Phenanthrenequinone (eq 3). The stannyl reagent **3** (179 mg, 0.48 mmol) was added to a dichloromethane solution (12 mL) of the quinone (83.2 mg, 0.4 mmol) and BF_3·OEt_2 (170 mg, 1.2 mmol) at −78 °C under N_2. The reaction mixture was warmed to −45 °C and then quenched with a saturated aqueous NaCl solution, followed by the usual workup. The product was isolated by preparative TLC, developing with 1:1 ether/hexane. The R_f 0.65 band contained 103 mg (88%) of γ-adduct **11**, pale yellow prisms: mp 133–135 °C; NMR ($CDCl_3$) δ 0.68, 1.25 (each m, 7 H, $CH_2CH_2CH_3$), 2.20 (m, 1 H, CH), 4.10 (s, 1 H, OH), 4.42–5.00 (m, 2 H, C=CH_2), 5.53 (m, 1 H, CH=C), 7.33–8.00 (m, 8 H, Ar H); IR (KBr) 3490, 2940, 1685, 1600, 1443, 1000, 920, 763, 730 cm^{-1}.

Anal. Calcd for $C_{20}H_{20}O_2$: C, 82.16; H, 6.89. Found: C, 81.77; H, 7.21.

The reaction with stannyl reagent **4** was performed according to the same procedure described above. Workup afforded **11** (73 mg, 63%).

Reactions of Neryltributylstannane (5) and Geranyltributylstannane (6) with Quinones. A. The stannyl reagent **5** was added to 1,2-naphthoquinone, **1a**, and BF_3·OEt_2 in CH_2Cl_2 at −78 °C, followed by the general reaction procedure. After acetylation, the product was isolated and purified by preparative TLC (developing twice with 3:2 ether/hexane) to afford **12**: 66% $\Delta^{2'}$-*Z*; a pale yellow oil; NMR (CCl_4) δ 1.60 (s, terminal *trans*-CH_3), 1.66 (s, *cis*-CH_3), 1.74 (s, CH_3 nearest ring), 2.16 (br, CH_2CH_2), 2.23 (s, $OCOCH_3$), 2.35 (s, $OCOCH_3$), 3.75 (d, CH_2, *J* = 8 Hz), 5.42 (m, olefinic H), 7.27–8.15 (m, Ar H); IR ($CHCl_3$) 2950, 2925, 1770, 1605, 1458, 1365, 1187 cm^{-1}.

B. The stannyl reagent **6** was added to **1a** and BF_3·OEt_2 in CH_2Cl_2 at −78 °C, followed by the general procedure. After acetylation, the product was isolated by preparative TLC (developing twice with 3:2 ether/hexane) to afford **12**: 95% $\Delta^{2'}$-*E*.

C. The stannyl reagent **5** was added to *p*-benzoquinone, **2a**, and BF_3·OEt_2 in CH_2Cl_2 at −78 °C, followed by the general procedure. After acetylation, the product was isolated and purified by preparative TLC (developing with chloroform) to afford **13**: 68% $\Delta^{2'}$-*Z*; oil; NMR (CCl_4) δ 1.54 (s, terminal *E*-CH_3), 1.60 (s, *Z*-CH_3), 1.71 (s, CH_3 nearest ring), 2.04 (s, CH_2CH_2), 2.13 (s, $OCOCH_3$), 2.15 (s, $OCOCH_3$), 3.12 (d, CH_2, *J* = 7 Hz), 5.05 (m, olefinic H), 6.78 (m, Ar H); IR ($CHCl_3$) 2952, 2920, 1758, 1485, 1365, 1168, 1010 cm^{-1}.

D. The stannyl reagent **6** was added to **2a** and BF_3·OEt_2 in CH_2Cl_2 at −78 °C, followed by the general procedure. After acetylation, the product was isolated by preparative TLC (developing with chloroform) to afford **13**: 96% $\Delta^{2'}$-*E*; oil.

E. The stannyl reagent **5** was added to 2-methyl-1,4-naphthoquinone, **2d**, and BF_3·OEt_2 in CH_2Cl_2 at −78 °C, followed by the general procedure. After oxidation with Ag_2O, the product was isolated and purified by preparative TLC, developing twice with 2:3 ether/hexane. The R_f 0.78 band contained vitamin $K_{2(10)}$: 67% $\Delta^{2'}$-*Z*; all spectral data were coincident with the reported values.[2c]

F. The stannyl reagent **6** was added to **2d** and BF_3·OEt_2 in CH_2Cl_2 at −78 °C, followed by the general procedure. After oxidation with Ag_2O, the product was isolated by preparative TLC, developing with 3:7 ether/hexane. The R_f 0.77 band contained vitamin $K_{2(10)}$: 97% $\Delta^{2'}$-*E*; all spectral data were coincident with the reported values.[1a,2c]

Reactions of 5 and 6 with 9,10-Phenanthrenequinone (eq 4). The stannyl reagent **5** (154 mg, 0.36 mmol) was added to a CH_2Cl_2 (12 mL) of the quinone (62.4 mg, 0.3 mmol) and BF_3·OEt_2 (128 mg, 0.9 mmol) at −78 °C under N_2. The reaction mixture was warmed to −50 °C and then quenched with a saturated aqueous NaCl solution (3 mL), followed by the usual workup. The product was isolated and purified by preparative TLC, developing twice with 1:4 ether/hexane. The R_f 0.70 band contained 56 mg (54%) of **14**: a pale yellow oil; NMR (CCl_4) δ 1.20, 1.48, 1.58, 1.69 (each s, total 9 H, side chain CH_3), 1.87 (br, 4 H, CH_2CH_2), 2.44 (d, 2 H, $ArCH_2$, *J* = 8 Hz), 3.97 (s, 1 H, OH), 4.98 (br m, 2 H, olefinic H), 7.30–8.00 (m, 8 H, Ar H); IR (CCl_4) 3500 (OH), 2960, 2910, 1692, (C=O), 1600, 1450 cm^{-1}.

Anal. Calcd for $C_{24}H_{26}O_2$: C, 83.20; H, 7.56. Found: C, 83.51; H, 7.71.

The reaction of stannyl reagent **6** (205 mg, 0.48 mmol) with 9,10-phenanthrenequinone (83.2 mg, 0.4 mmol) in the presence of BF_3·OEt_2 (170 mg, 1.2 mmol) was performed according to the same procedure described above. Workup as above afforded **14** (85 mg, 62%).

Directed Alkyl Substitution of the Dodecahedrane Nucleus. The 1,4-Dimethyl, 1,6-Dimethyl, and 1,4,16-Trimethyl Derivatives. Indanododecahedrane by Stepwise Dehydrogenation of a Benzylated Seco Derivative

Leo A. Paquette* and Yuji Miyahara

Evans Chemical Laboratories, The Ohio State University, Columbus, Ohio 43210

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A 1:1 mixture of finely divided titanium metal and 5% platinum on alumina catalyzes the dehydrocyclization of secododecahedrane **3** to 1,6-dimethyldodecahedrane (**4**). A small quantity (10–15%) of the monomethyl derivative is coproduced. This demethylation process could be used to synthetic advantage when applied to the trimethyl-substituted secododecahedrane **11**, the synthesis of which is first detailed. Heating **11** with the catalyst system at 200 °C (two passes of 36-h duration) affords 1,3,16-trimethyldodecahedrane (**12**) and the 1,4-dimethyl derivative (**13**). These hydrocarbons were separated by fractional crystallization and characterized spectroscopically. The spectral properties of the three known dimethyldodecahedranes are correlated. A preparation of benzylsecododecahedrane **26** is also detailed. Heating of **26** at 200 °C with the preceding catalyst system leads efficiently to benzyldodecahedrane. Stepwise dehydrogenation has also proven feasible as shown by independent conversion to 2,3-indanododecahedrane at 260 °C. The ready formation of a 1,2-disubstituted dodecahedrane is thereby demonstrated.

Historical documentation of attempts by organic chemists to prepare dodecahedrane is rich and varied.[1] The central importance of the polycyclopentanoid $(CH)_{20}$ array that characterizes this molecule has fostered the development of many creative strategies, only one of which has been sucessful to date. In 1981, we reported acquisition of the 1,16-dimethyl derivative and detailed its three-di-

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