Allylation of Quinones via Photoinduced Electron-Transfer Reactions from Allylstannanes

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Photochemical reactions of quinones with allylstannanes provided four types of products: adducts of allyl group to the carbonyl oxygens of quinones, adducts of allyl group to the olefinic carbons, adducts of allyl group to the carbonyl carbons, and hydroquinones. An electron-transfer mechanism was confirmed by ^{1}H-CIDNP (Chemically Induced Dynamic Nuclear Polarization) method. This study suggests that a) photoinduced electron transfer from allylstannanes to quinones produces the corresponding quinone anion radicals and tin cation radicals, b) the tin cation radicals cleave to give allyl radicals as well as tin cation, and c) the allyl radicals attack the quinone anion radicals resulting in the formation of final products, allylated quinones.

During the last decade the photostimulated electron-transfer reactions have been a topic in organic photochemistry.[1] One-electron transfer from donor to acceptor results in the formation of ion radical pair followed by the secondary reactions to produce final products. Efficacy of the secondary reactions; however, is controlled by the rate of back electron transfer. Many efforts to reduce the back electron transfer have been done so far. One of the way to solve this problem is the use of stabilized radical species generated by fragmentation of the cation radicals (Scheme 1). This process has been realized in the photooxidation of acid,[2] alcohol,[3] ether,[3] amine,[4] olefin,[5] silane,[6,7] stannane,[8–11] and so on[12] accompanied with the subsequent loss of a cation or a proton.

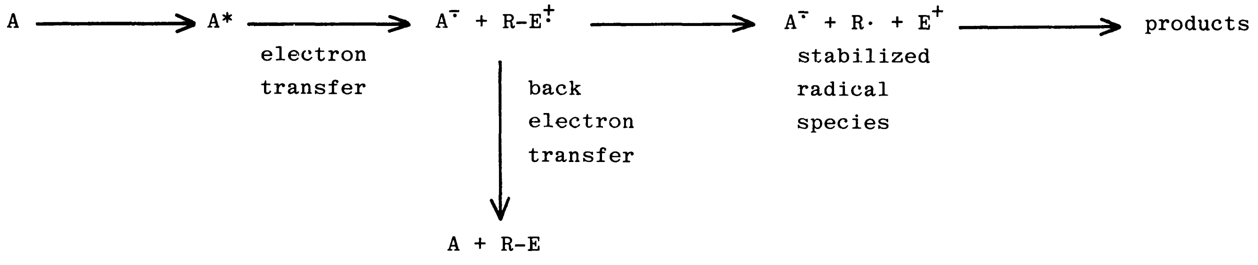
Mariano[6] and Mizuno[7] reported photoaddition reactions related to the allylsilane–iminium salt and allylsilane-cyano aromatics which were initiated by one-electron transfer and subsequent cleavage of silane cation radical to allyl radical and silane cation. However, only a few photochemical reactions of allyltin reagents have been reported.[8–11]

Allylation of quinones[13–15] is a major route for preparing isoprenoid quinones,[16] which play an important role in several metabolic sequences as well as being a key step in synthesis of antitumor-antibiotic quinonoid compounds.[17] It has been proved that allyl 4B metal compounds, allylsilane[14] and allylstannane,[15] are excellent reagents for direct introduction of allyl group to quinonoid nucleus. Thermal reactions of quinones with allylstannanes in the presence of a Lewis acid, especially BF_3, was of the most effective for allylation of quinones.[15] There have been a lot of reports on these thermal allylation of quinones, while by our knowledge one communication has appeared on photoallylation of quinones with allylsilane,[18] and no report on photoallylation of quinones with allylstannanes.

To explore the synthetic utility of the photochemistry of quinones with allylstannanes and to clarify the difference between thermal and photochemical reactions including the difference of reactivities between allylsilane and allylstannane, we have attempted to study the photochemistry of allylstannane–quinone systems. Now we will discuss the photochemistry of quinones with allylstannanes in this paper.

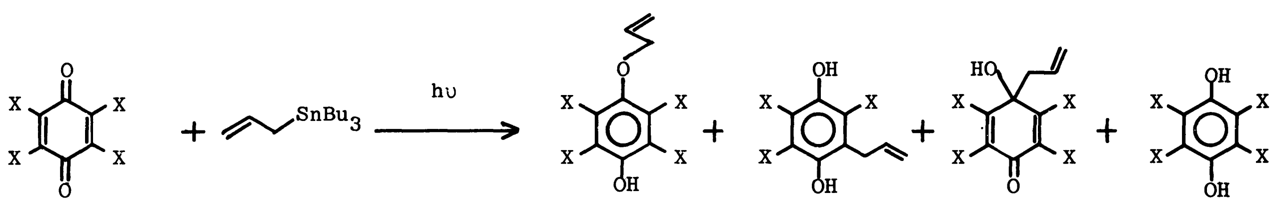
Results

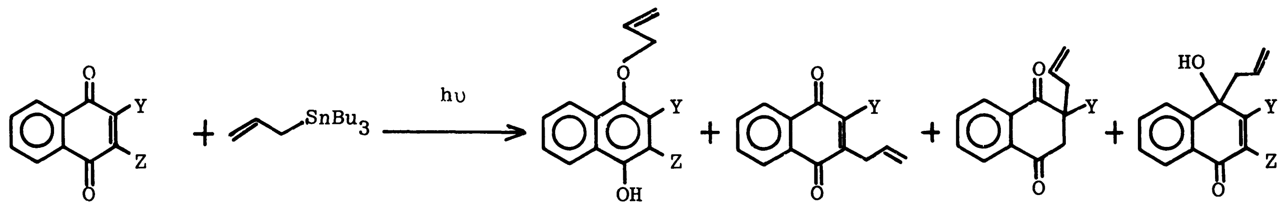
Photochemical Reactions between Quinones and Allyltributylstannane. Photochemical reactions of a variety of quinones with allyltributylstannane were investigated. Irradiation of a benzene solution (25 ml) containing chloranil **1a** (1 mmol) and allyltributylstannane **2a** (2 mmol) with a high-pressure mercury lamp through an aqueous $CuSO_4$ filter ($h\nu$>315 nm) for 3 h under argon afforded a mixture of 4-allyloxy-



Scheme 1.

2,3,5,6-tetrachlorophenol **3a** (20%), 4-allyl-2,3,5,6-tetrachloro-4-hydroxy-2,5-cyclohexadien-1-one **7a** (20%), and 2,3,5,6-tetrachloro-1,4-benzenediol **8a** (50%). The yields of the respective products were based on the consumed quinone **1**. Likewise, **3a** (28%), **7a** (14%), and **8a** (12%) were obtained in acetonitrile (Run 2), but with different product distribution compared to the reaction in benzene. Structures of the products were readily assigned from the ^{1}H NMR, IR, mass spectroscopy, elemental analyses, suitable chemical transformations, and comparisons with those of structually related substances.[15] The IR spectrum of **3a** showed characteristic band due to hydroxyl group at 3430 cm^{-1}, while that of **7a** showed characteristic bands due to carbonyl and hydroxyl group at 1665 and 3400 cm^{-1}, respectively. In the mass spectrum of **3a** parent peaks appeared at m/z 286, 288, 290, 292, 294, indicating that one propene moiety had been incorporated into **1a**. In its ^{1}H NMR spectrum the α proton signal of allyl group in **3a** appeared at 4.53 as a doublet, while that of **7a** was at 2.97 as a doublet. Compound **3a** was compared with the authentic sample obtained by independent synthesis (see Experimental section). The results of photochemical reactions of quinones **1a—h** with allylstannane **2a** are summarized in Table 1. In the case of benzoquinone **1b** (Run 3), hydroquinone **8b** (52%) was major product besides yielding 4-(allyloxy)phenol **3b** (26%) and 2-allylhydroquinone **4b** (6%). On the other hand, naphthoquinone derivatives gave no 1,4-naphthalenediol (Runs 5—16). In the case of 2,3-dibromo-1,4-naphthoquinone **1c**, 2-allyl-3-bromo-1,4-naphthoquinone **5c** (29%) and 4-allyl-4-hydroxy-1(4*H*)-naphthalenone (designated to allyl quinol, hereafter) **7c** (28%) were obtained. The IR spectrum of **5c** showed characteristic bands due to carbonyl group at 1665 cm^{-1}, while that of **7c** showed those due to carbonyl and hydroxyl group at 1650 and 3360 cm^{-1}, respectively. In the mass





Scheme 2.

Table 1. Photochemical Reactions of Quinones **1** with Allyltributylstannane (**2a**)

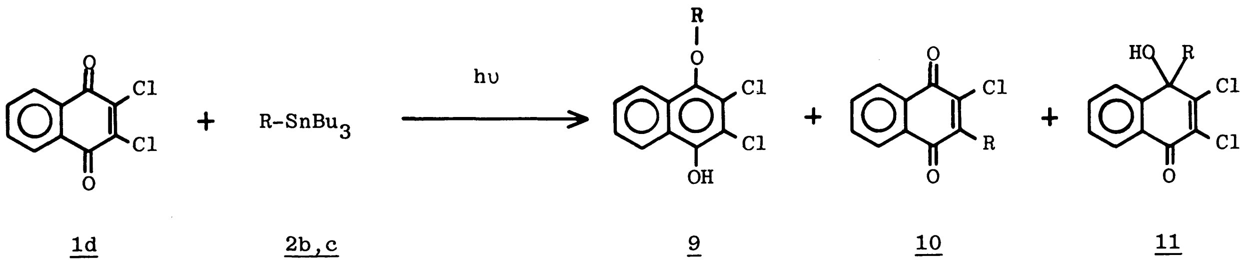
Run	Quinone	Solvent	Conversion/%[a]	Products (yield/%)[b]
1	**1a**: X=Cl	C_6H_6	100	**3a**: X=Cl (20); **7a**: X=Cl (20); **8a**: X=Cl (50)
2	**1a**: X=Cl	CH_3CN	100	**3a**: X=Cl (28); **7a**: X=Cl (14); **8a**: X=Cl (12)
3	**1b**: X=H	C_6H_6	100	**3b**: X=H (26); **4b**: X=H (6); **8b**: X=H (52)
4	**1b**: X=H	CH_3CN	100	**3b**: X=H (23); **4b**: X=H (13); **8b**: X=H (57)
5	**1c**: Y=Z=Br	C_6H_6	75	**5c**: Y=Br (29); **7c**: Y=Z=Br (28)
6	**1c**: Y=Z=Br	CH_3CN	66	**5c**: Y=Br (47); **7c**: Y=Z=Br (32)
7	**1d**: Y=Z=Cl	C_6H_6	74	**5d**: Y=Cl (35); **7d**: Y=Z=Cl (15)
8	**1d**: Y=Z=Cl	CH_3CN	100	**5d**: Y=Cl (12); **7d**: Y=Z=Cl (26)
9	**1e**: Y=Br, Z=H	C_6H_6	81	**5c**: Y=Br (9); **5e**: Y=H (20)
10	**1e**: Y=Br, Z=H	CH_3CN	97	**5c**: Y=Br (15); **5e**: Y=H (15)
11	**1f**: Y=Z=H	C_6H_6	70	**3f**: Y=Z=H (21); **5e**: Y=H (14); **7f**: Y=Z=H (29)
12	**1f**: Y=Z=H	CH_3CN	98	**3f**: Y=Z=H (21); **5e**: Y=H (10); **7f**: Y=Z=H (11)
13	**1g**: Y=CH_3, Z=H	C_6H_6	78	**5g**: Y=CH_3 (38); **6g**: Y=CH_3 (28); **7g**: Y=H, Z=CH_3 (26)
14	**1g**: Y=CH_3, Z=H	CH_3CN	85	**5g**: Y=CH_3 (15); **6g**: Y=CH_3 (35); **7g**: Y=H, Z=CH_3 (32)
15	**1h**: Y=OCH_3, Z=H	C_6H_6	70	**5h**: Y=OCH_3 (53); **7h**: Y=OCH_3, Z=H (37)
16	**1h**: Y=OCH_3, Z=H	CH_3CN	50	**5h**: Y=OCH_3 (34); **7h**: Y=OCH_3, Z=H (56)

a) Irradiated for 3 h except Run 8 (35 h). b) Isolated yield based on a starting quinone consumed.

spectrum of **5c** parent peaks appeared at m/z 276, 278, indicating incorporation of one allyl group into **1c** and lose of one bromine atom from **1c**. In its ^{1}H NMR spectrum the α proton signal of allyl group in **5c** appeared at 3.66 as a doublet, while that of **7c** showed diastereotopic methylene at 2.70 (1H, dd, J=6, 13 Hz), 3.02 (1H, dd, J=6, 13 Hz). Similarly, 2,3-dichloro-1,4-naphthoquinone **1d** gave allyl quinone **5d** (35%) and allyl quinol **7d** (15%) (Run 7). 2-Bromo-1,4-naphthoquinone **1e**, however, gave no allyl quinol, but allyl quinones **5c** (9%) and **5e** (20%) were the products. Naphthoquinone **1f** gave all possible products, allyl ether **3f** (21%), allyl quinone **5e** (14%), and allyl quinol **7f** (29%). Reactions of unsymmetrical quinones, 2-methyl-1,4-naphthoquinone **1g** or 2-methoxy-1,4-naphthoquinone **1h**, gave allyl quinone **5g** (38%), 2-allyl-2,3-dihydro-1,4-naphthalenedione (abbreviated to allyl dione, hereafter) **6g** (28%), and allyl quinol **7g** (26%) (Run 13), or allyl quinone **5h** (53%) and allyl quinol **7h** (37%), respectively (Run 15). The ^{1}H NMR of allyl dione **6g** showed two pairs of diastereotopic methylene at δ 2.29 (1H, dd, J=7, 14 Hz), 2.61 (1H, dd, J=7, 14 Hz), 2.85 (1H, d, J=17 Hz), 3.10 (1H, d, J=17 Hz), and the ^{13}C NMR of **6g** showed carbonyl carbons at δ 196.0, 200.1. Surprisingly, in the cases of **1g** and **1h**, the corresponding allyl quinols **7g** and **7h**, were formed regioselectively.[19] Assignment of the regiochemistry was as follows. Since the ^{13}C NMR shift of β carbon in α,β-unsaturated ketone is characteristic, the signals appeared at δ 135.8 and 145.5 due to C2 and C3 may be assigned to 2-methyl-2-cyclohexen-1-one, while those appeared at δ 126.5 and 162.2 due to C2 and C3 to 3-methyl-2-cyclohexen-1-one, respectively. The ^{13}C NMR signals of **7g** due to C2 and C3 appeared at δ 129.9 and 147.1, respectively, which were determined by off-resonance decoupling of ^{13}C NMR spectroscopy and two dimensional ^{13}C–^{1}H shift correlation NMR spectroscopy. The structure of **7h** was assigned by comparison with the previously reported data.[15] Some of allyl quinols and allyl ethers were fairly unstable, and then after the hydroxyl group of them were acetylated the structure were confirmed (see Experimental section). In all cases, product distributions were quite dependent on solvents; benzene or acetonitrile, but there was no consistent inclinations.

Photochemical Reactions of 2,3-Dichloro-1,4-naphthoquinone with Prenyl (or Benzyl) Tin Reagents. The photochemical reactions of **1d** (1 mmol) with (3-methyl-2-butenyl)tributylstannane **2b** or benzyltributylstannane **2c** (2 mmol) were carried out in benzene (25 ml). As expected, three classes of products were obtained in both cases; compounds **9**, **10**, and **11**, which were also assigned by spectroscopic data and chemical transformation (see Experimental section). In the reaction of prenylstannane **2b**, prenyl ether **9b** (27%), prenyl quinone **10b** (27%), and prenyl quinol **11b** (19%) having α adduct structures were obtained exclusively[20] (Scheme 3). This method will provide a feasible route of isoprenoid quinones, which play an important role in biological electron transfer. Similarly, the photochemical reaction of **1d** with benzylstannane **2c** gave benzyl ether **9c** (26%), benzyl quinone **10c** (36%), and benzyl quinol **11c** (23%).

Mechanistic Aspects of the Reactions. To clarify the reaction mechanism, we have applied ^{1}H-CIDNP method to the photochemical reactions.[10] When a benzene-d_6 solution of **1d** ($\approx 10^{-2}$ mol dm^{-3}) and **2a** ($\approx 10^{-2}$ mol dm^{-3}) was irradiated (>330 nm) under argon, strong ^{1}H-CIDNP signals due to the allyl quinone **5d** and the by-product, 1,5-hexadiene **12a**, which were assigned by comparison with the authentic samples, were observed (Fig. 1). In acetonitrile-d_3 similar but weaker polarizations were observed. These polarizations are explained reasonably by the Kaptein's rule (See Ref. 21 for the polarization signals due to **5d** and **12a**). In the reaction of **1c** with **2a**, similar polarizations of allyl quinone **5c** and diene **12a** were observed in benzene-d_6, and furthermore in that of **1e** with **2a**, polarization signals due to allyl quinones **5c**,



Stannane	Conversion/%[a]	Products (yield %)[b]		
2b: R=$CH_2CH=C(CH_3)_2$	73	**9b**: (27)	**10b**: (27)	**11b**: (19)
2c: R=CH_2Ph	84	**9c**: (26)	**10c**: (36)	**11c**: (23)

a) Irradiated for 3 h in benzene. b) Isolated yield based on a starting quinone consumed.

Scheme 3.

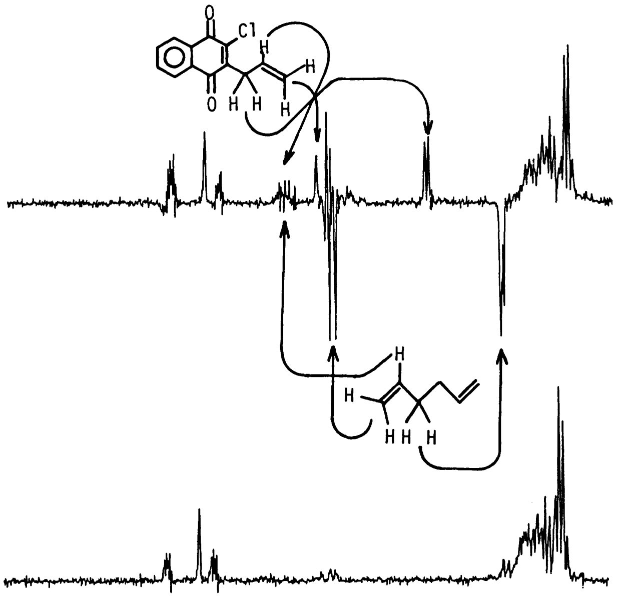


Fig. 1. ^{1}H NMR spectra (100 MHz) of a benzene-d_6 solution containing **1d** and **2a** in the dark (bottom) and during irradiation (top).

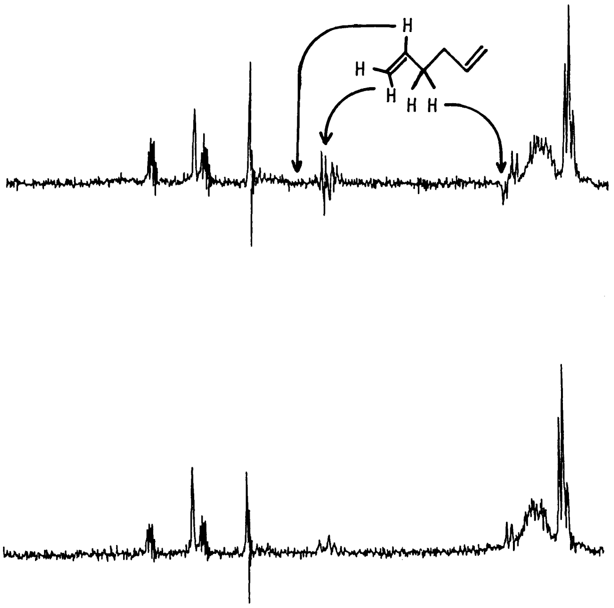


Fig. 2. ^{1}H NMR spectra (100 MHz) of a benzene-d_6 solution containing **1f** and **2a** in the dark (bottom) and during irradiation (top).

5e and diene **12a** were observed. But in the reactions of **1f** or **1g** with **2a**, only polarization signals due to **12a** were observed in benzene-d_6 (Fig. 2). None of the polarizations were observed in the reactions of **1b** or **1h** with **2a** in benzene-d_6. On the other hand in the reaction of **1a** with **2a**, the strongest polarizations due to both an adduct and diene **12a**, were observed in benzene-d_6, but the polarization due to the adduct could not be assigned to the final products, **3a**, **7a**, and

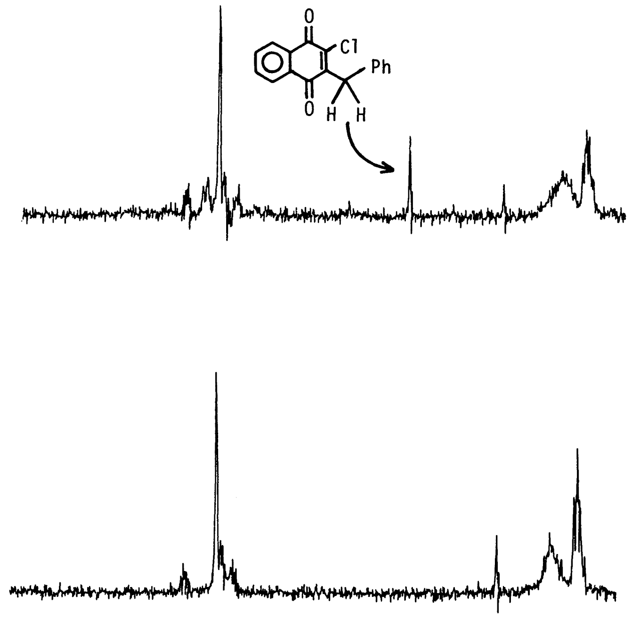


Fig. 3. ^{1}H NMR spectra (100 MHz) of a benzene-d_6 solution containing **1d** and **2c** in the dark (bottom) and during irradiation (top).

8a. In the reaction of **1d** with **2b**, ^{1}H NMR polarizations of allyl quinone **10b** were observed in benzene-d_6,[22] but polarizations based on other by-products; i.e, 2,7-dimethyl-2,6-octadiene, were not verified because of the complex signal derived from $-SnBu_3$ group. In the reaction of **1d** with **2c**, the polarization signals due to benzyl quinone **10c** were observed in benzene-d_6[23] (Fig. 3). In all of the CIDNP experiments, same pattern of polarization signals were observed in the reactions of both benzene-d_6 and acetonitrile-d_3 solution, but, in general, polarizations in benzene were stronger than that in acetonitrile.

Discussion

The free energy changes in electron-transfer process from a tin reagent to excited triplet quinone can be estimated by Rehm–Weller equation[24] (Eq. 1), where $E_{1/2}{}^{ox}$ and $E_{1/2_{red}}$ are redox potential of the electron donors and acceptors, respectively. $\Delta E_{0,0}$ is the excitation energy of **1**, and C represents the Coulomb term.

$$\Delta G(\text{kcal mol}^{-1})=23.06(E^{ox}_{1/2} - E^{red}_{1/2} + C) - \Delta E_{0,0} \quad (1)$$

(1 cal = 4.184 J)

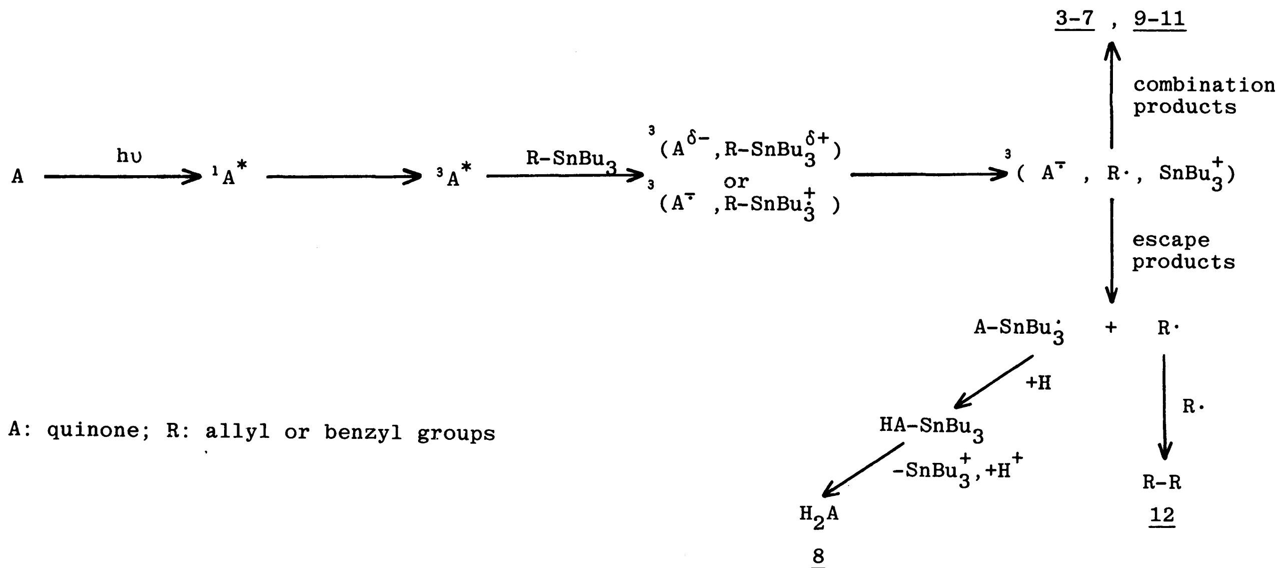
We assume that the Coulomb term is too small to influence the present reactions. The reported or measured values of $E^{ox}_{1/2}$,[7] $E^{red}_{1/2}$,[25,26] and $\Delta E_{0,0}$[16b,27] were used for calculating the values of ΔG (see Table 2). The calculated values of ΔG were all negative, indicating that the electron transfer was possible.

Direct unambiguous evidences for electron-transfer processes were obtained by CIDNP method. It is noteworthy that with some exceptions polarizations in the forward reaction path, but not in the reverse one, were observed. That is, polarizations due to both allyl quinone **5** and dimerization product of allyl radical **12a** were observed simultaneously in the reactions of **1c—e** with **2a**, whereas in many other photoinduced electron-transfer processes such as the reactions between quinones and 1,1-diarylethylenes[25] polarizations due to starting reactants based on the back electron transfer used to be observed. On the contrary, in the reactions of quinones **1f** or **1g**, only polarizations due to **12a** were observed, and in addition, no polarizations were observed in the reactions of quinones **1b** or **1h**. These quinones, i.e., **1b**, **1f—h**, have relatively low reduction potential. Therefore, an appreciable amount of polarizations would not be observed, because of the insufficient electron transfer in an unit time. This correlation between CIDNP polarizations and reduction potentials of quinones is another support of the electron-transfer processes in this system. Result of CIDNP in the reaction of **1a** with **2a** is interesting, polarizations of unstable adduct are quite strong and similar to those due to allyl quinones, but the adduct could not be isolated.[29]

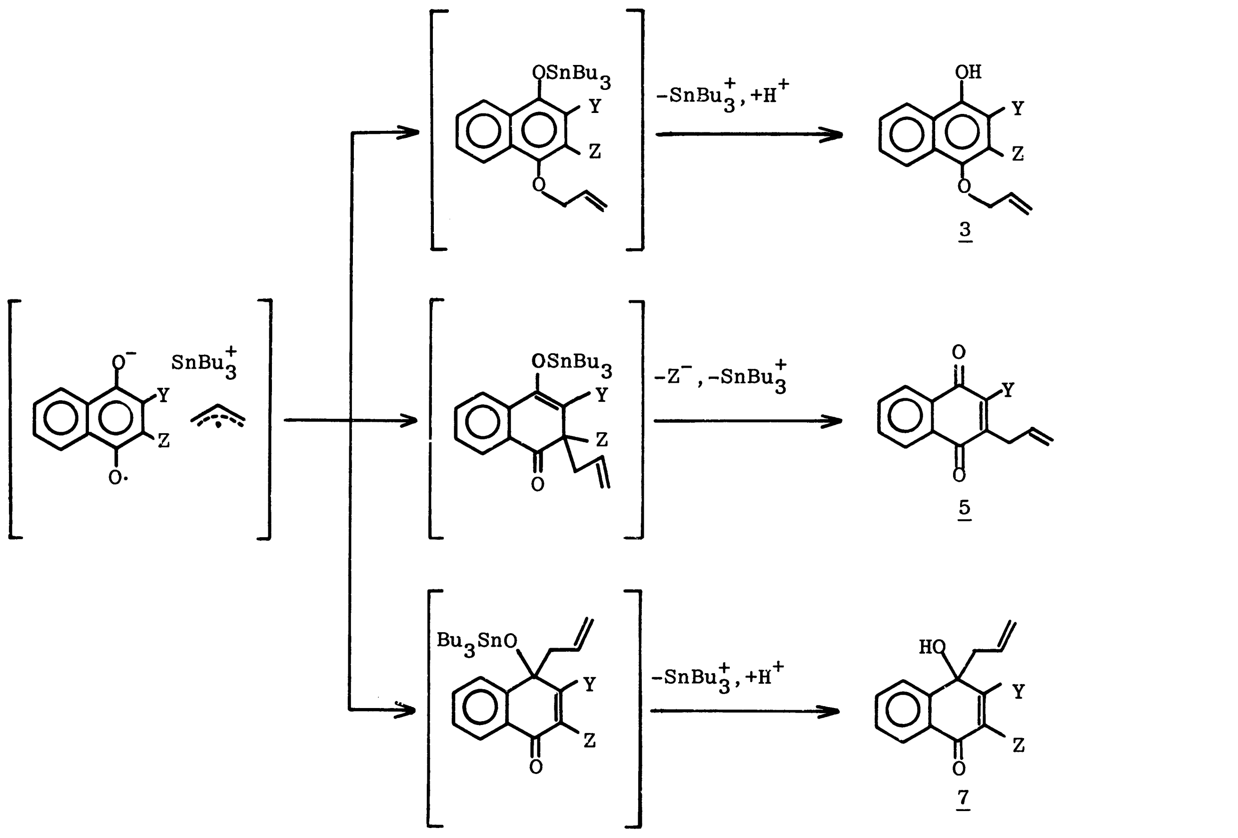
In the reaction of **1d** with **2b**, polarizations due to prenyl quinone and possibly dimerization product of prenyl radical were observed similar to the reaction of **1d** with **2a**, but in the reaction of **1d** with **2c** only corresponding polarizations due to adduct **10c** were observed. But trace amount of 1,2-diphenylethane, dimerization product of benzyl radical, (GLC<1%) was detected in the photoproduct. Thus, the photochemical reactions of quinones with benzyltrialkylstannane as well as allyltrialkylstannane could proceed by electron-transfer mechanism.

On the basis of these findings, we propose an electron-transfer mechanism[30] shown in Scheme 4. This is analogous to the well-established mechanism for the iminium salt-allylsilane photochemical reaction.[6] Because of the strong oxidizing power of quinones and lower oxidation potential of allyl or benzylstannanes as compared to allylsilane, electron transfer easily occurs from tin reagent to excited triplet quinone,[31] producing the ion radical pair ($1^{\overline{\cdot}}$, $2^{\dagger}$), but in nonpolar solvent the corresponding intermediate may be an exciplex.[32] Owing to the instability of $2^{\dagger}$,[33] allyl or benzyl radical may cleave from the tin cation radical, forming triplet ion radical pair ($1^{\overline{\cdot}}$, R·, $SnBu_3^{+}$)^{T} subsequently. Attack of allyl or benzyl radical toward quinone anion radical $1^{\overline{\cdot}}$ followed by bonding with tin cation could give the corresponding intermediates, which lead to formation of the adducts **3—7**, **9—11** (Scheme 5). Quinone anion radical and allyl radical escaped from the solvent cage would give reduction product, hydroquinone **8**,[34] and the dimerization product **12** of allyl or benzyl radical.[35]

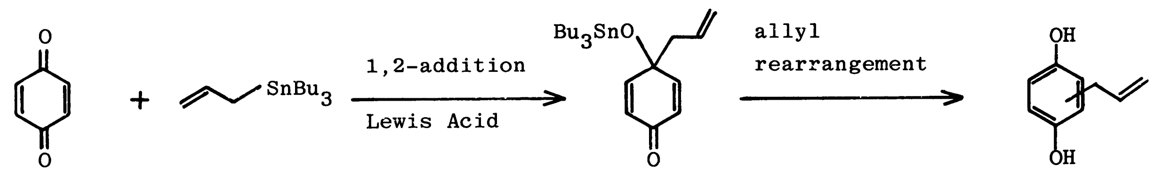
In the reactions of **1** with **2a**, conversion of reactions decreased as decrease of the reduction potential of quinones, suggesting the electron-transfer processes in the reactions. There is a tendency that allylations occur at almost all positions of quinones,[36] because spin densities of quinone anion radical are rather similar at all positions.[37,38] It is noteworthy, however, that allyl quinols **7g** and **7h** were formed regioselectively. Probably both steric hindrance of alkyl tin moiety against methyl group in **1g** and coordination of tin to the methoxyl group in **1h** affect the regioselective formation of **7g** and **7h**. In the reaction of **1d** with **2b**, it gave α adducts exclusively. The regioselectivity of the addition (α or γ addition) of allylic moiety may be influenced by steric hindrance between methyl groups in prenyl radical and func-



Scheme 4.



Scheme 5.



Scheme 6.

tional group in quinone.

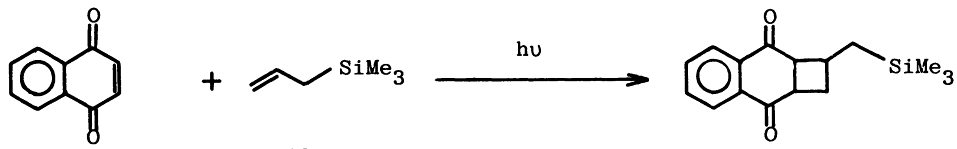
Comparison of Other Related Reactions. In the thermal reactions allylation of quinones requires Lewis acids, e.g., BF_3, as catalyst, but in the photochemical reactions none of Lewis acids, of course, is required except with electronic activation of quinones. As the result of the mechanistic study of the thermal reaction between quinone and allyltin reagent in the presence of a Lewis acid, it was established that allylation of quinones proceeds via 1,2-addition followed by allyl rearrangement[15] (Scheme 6). Allyl quinol **7** obtained in the photoreaction of quinones with allylstannane is fairly stable once purified but gradually rearranges to give allyl quinone **5**. In fact, photoproduct **7d** could be transformed to **5d** in refluxing benzene for 2 days (75%), as reported previously.[15] On the contrary, **7d** underwent no photochemical reaction for 4 h, indicating that the same mechanism for the thermal allylation does not occur in the photoreaction.

Fujita et al.[18] reported that in the photochemical reactions of quinones with allylsilane **13**, $[2\pi+2\pi]$ cyclobutane adducts were obtained as sole photoproduct (Scheme 7). To compare the difference in their reactivity between allylsilane and allylstannane, photo-CIDNP examination of quinone–allylsilane systems was carried out, but no polarizations were observed in the photochemical reactions of **1f** with **13** and even in the reaction of **1d** with **13**. This phenomena suggests that efficient electron transfer from **13** to quinones does not occur. Equation 1 allows us to estimate ΔG for photoinduced electron transfer from **13** to quinones **1** (Table 2). Much larger values of ΔG compared with the allylstannane–quinone systems, reflecting the higher oxidation potential of allylsilane, also support the inefficient electron-transfer process in the latter systems. Thus, in the reported photochemical reactions of allylsilane, only [2+2] cyclobutane adduct would be formed, while in those of allylstannane a variety of allylation

Table 2. Redox Potentials, Triplet Energies, and Free Energy Changes

Quinone	$E^{red}_{1/2}$ (Ag/Ag+)	E^T/kcal mol^{-1}	Stannane or silane	$E^{ox}_{1/2}$ (Ag/Ag+)	ΔG/kcal mol^{-1}
1a	−0.23[a]	62[c]	**2a**	+0.88[f]	−36.4
1b	−0.75[a]	53[d]	**2a**		−15.4
1c	−0.77[b]	—	**2a**		−18.0[h]
1d	−0.77[b]	56[e]	**2a**		−18.0
1d			**2b**	+0.58[f]	−24.9
1d			**2c**	+0.90[f]	−17.5
1d			**13**	+1.58[g]	− 1.8
1e	−0.86[b]	—	**2a**		−15.9[h]
1f	−0.95[a]	58[d]	**2a**		−15.8
1f			**13**		+ 0.3
1g	−1.11[b]	58[d]	**2a**		−12.1
1h	−1.15[b]	—	**2a**		− 9.2[h]

a) From Peover[26] and assumed that potential against Ag/Ag+ is 0.24 V lower than that measured against SCE.[28] b) From our work.[25] c) From Kasha.[27] d) From Ref. 16b. e) Determined by measurement of phosphorescence spectra. f) Measured in CH_3CN with Et_4NClO_4 as supporting electrolyte vs. Ag/Ag+. g) From Mizuno.[7] h) Assumed that the value of E^T is 56 kcal mol^{-1}.



Scheme 7.

products of quinones could be produced via electron transfer including radical processes.

Experimental

General Procedures. All melting points were determined with a Yanagimoto micro melting point apparatus and uncorrected. Mass spectra were taken on a JEOL JMS-DX300 mass spectrometer. The electronic spectra were obtained by Shimadzu UV-200 spectrometer. ^{1}H NMR spectra were taken by using a JEOL JNM-PS-100 spectrometer or JEOL JNM-GX-400 spectrometer and chemical shifts were recorded in parts per million (ppm) on the δ scale from tetramethylsilane as an internal standard, while ^{13}C NMR spectra were taken by using JEOL JNM-GX-400 spectrometer. IR spectra were obtained by using a JASCO IRA-1 spectrometer on KBr pellets or liquid film on NaCl. Gas chromatography analyses were carried out by using JEOL-1100. Fluorescence and phosphorescence spectra were taken by using a Shimadzu RF-502A spectrometer. Elemental analyses were performed at the Micro Analytical Center of Kyoto University. Cyclic voltammetry was performed with a PAR Model 174. The working electrode was platinum wire. A Ag/Ag+ (0.1 M; 1 M=1 mol dm^{-3}) electrode was used as a reference electrode and 0.1 M tetraethylammonium perchlorate as supporting electrolyte.

In general, irradiation of a benzene or an acetonitrile solution (25 ml) containing quinone (1 mmol) and tin reagent (2 mmol) through an aqueous $CuSO_4$ and a Pyrex filter under argon are carried out at room temperature. After irradiation the reaction mixture is concentrated and separated by flash column chromatography on silica gel (Merck kiesel gel 60H), developing with hexane–benzene, benzene subsequently, and chloroform finally. The first band contains allylstannanes **2**, the second one contains allyl ether **3**, the third one contains allyl quinones **5** (**4**, **6**), the fourth one contains quinone **1**, the fifth one contains allyl quinol **7**, and the final one contains hydroquinone **8**.

Starting Materials. Chloranil **1a** benzoquinone **1b**, 2,3-dichloro-1,4-naphthoquinone **1d**, 1,4-naphthoquinone **1f**, and 2-methyl-1,4-naphthoquinone **1g** were commercially available and were purified by column chromatography, recrystallization, and sublimation. 2,3-Dibromo-1,4-naphthoquinone **1c**[39] and 2-bromo-1,4-naphthoquinone **1e**,[40] and 2-methoxy-1,4-naphthoquinone **1h**[41] were synthesized by the previous reported methods. Allyl and benzylstannanes **2a**—**c** were prepared by our previously reported method[42] and allyltrimethylsilane **13** was commercially available. Acetonitrile and benzene were used after distillation. Acetonitrile-d_3 and benzene-d_6 were commercially available and were used without further purification.

Physical Properties of the Products. 4-Allyloxy-2,3,5,6-tetrachlorophenol (**3a**): White plates from hexane–chloroform; mp 86.5—88.5 °C. MS; m/z 286, 288, 290, 292, 294 (M+). Found: C, 37.73; H, 1.99; Cl, 48.98%. Calcd for $C_9H_6O_2Cl_4$: C, 37.54; H, 2.10; Cl, 49.25%. IR (KBr); 3430 (OH) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=4.53 (2H, d, J=6 Hz), 5.3—5.6 (2H, m), 5.9—6.4 (2H, m). Compound **3a** was synthesized independently by the thermal allylation of the corresponding hydroquinone **8a** with K_2CO_3 and allyl bromide and the structure was confirmed.

4-(Allyloxy)phenol (3b): Colorless oil. High-resolution mass spectrum. Found: m/z 150.0685. Calcd for $C_9H_{10}O_2$: M, 150.0680. IR (NaCl); 3360 (OH) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=4.46 (2H, d, J=5 Hz), 5.1—5.5 (2H, m), 5.56 (1H, br-s), 5.8—6.2 (1H, m), 6.72 (4H, s).

4-Allyloxy-1-naphthol (3f): White needles from hexane–chloroform; mp 100—102 °C. MS; *m/z* 200 (M^+). Found: C, 77.94; H, 5.95%. Calcd for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04%. IR (KBr); 3230 (OH) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=4.52 (2H, d, *J*=5 Hz), 5.2—5.6 (2H, m), 5.9—6.4 (1H, m), 6.46 (1H, d, *J*=8 Hz), 6.67 (1H, d, *J*=8 Hz), 7.01 (1H, br-s), 7.3—8.3 (4H, m).

2-Allyl-3-bromo-1,4-naphthoquinone (5c): Yellow crystals from hexane–chloroform; mp 46—49 °C. High-resolution mass spectrum. Found: *m/z* 275.9787. Calcd for $C_{13}H_9O_2{}^{79}Br$: M, 275.9786. Found: *m/z* 277.9765. Calcd for $C_{13}H_9O_2{}^{81}Br$: M, 277.9767. IR (KBr); 1665 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=3.66 (2H, d, *J*=6 Hz), 5.1—5.5 (2H, m), 5.7—6.2 (1H, m), 7.84 (2H, m), 8.20 (2H, m).

2-Allyl-3-chloro-1,4-naphthoquinone (5d): Yellow needles from hexane–chloroform; mp 54—57 °C. High-resolution mass spectrum. Found: *m/z* 232.0293. Calcd for $C_{13}H_9O_2{}^{35}Cl$: M, 232.0291. Found: *m/z* 234.0256. Calcd for $C_{13}H_9O_2{}^{37}Cl$: M, 234.0261. IR (KBr); 1675 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=3.62 (2H, d, *J*=6 Hz), 5.0—5.5 (2H, m), 5.7—6.3 (1H, m), 7.87 (2H, m), 8.23 (2H, m).

2-Allyl-3-methyl-1,4-naphthoquinone (5g): Yellow oil. High-resolution mass spectrum. Found: *m/z* 212.0838. Calcd for $C_{14}H_{12}O_2$: M, 212.0837. IR (NaCl); 1660 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=2.17 (3H, s), 3.40 (2H, d, *J*=8 Hz), 5.0—5.1 (2H, m), 6.7—6.9 (1H, m), 7.6—7.8 (2H, m), 8.0—8.1 (2H, m).

2-Allyl-3-methoxy-1,4-naphthoquinone (5h): Yellow oil. High-resolution mass spectrum. Found: *m/z* 228.0784. Calcd for $C_{14}H_{12}O_3$: M, 228.0783. IR (NaCl); 1660 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=3.33 (2H, d, *J*=7 Hz), 4.11 (3H, s), 4.9—5.3 (2H, m), 5.6—6.1 (1H, m), 7.5—7.7 (2H, m), 7.9—8.1 (2H, m).

2-Allyl-2,3-dihydro-2-methyl-1,4-naphthalenedione (6g): Yellow oil. High-resolution mass spectrum. Found: *m/z* 214.0989. Calcd for $C_{14}H_{14}O_2$: M, 214.0994. IR (NaCl); 1680 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=1.30 (3H, s), 2.29 (1H, dd, *J*=7, 14 Hz), 2.61 (1H, dd, *J*=7, 14 Hz), 2.85 (1H, d, *J*=17 Hz), 3.10 (1H, d, *J*=17 Hz), 4.9—5.3 (2H, m), 5.6—6.1 (1H, m), 7.7—7.9 (2H, m), 8.0—8.2 (2H, m). ^{13}C NMR ($CDCl_3$) δ=23.5, 42.6, 48.4, 49.2, 119.2, 125.8, 127.2, 132.4, 133.5, 133.7, 134.1, 134.6, 196.0, 200.1.

4-Allyl-2,3,5,6-tetrachloro-4-hydroxy-2,5-cyclohexadien-1-one (7a): White needles from hexane–chloroform; mp 88—90.5 °C. MS; *m/z* 286, 288, 290, 292, 294 (M^+). Found: C, 37.56; H, 2.11; Cl, 49.03%. Calcd for $C_9H_6O_2Cl_4$: C, 37.54; H, 2.10; Cl, 49.25%. IR (KBr); 3400 (OH), 1665 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=2.97 (2H, d, *J*=6 Hz), 4.41 (1H, br-s), 5.0—5.5 (3H, m).

4-Allyl-2,3-dibromo-4-hydroxy-1(4*H*)-naphthalenone (7c): White crystals from hexane–chloroform; mp 88—91 °C. MS; *m/z* 356, 358, 360 (M^+). IR (KBr); 3360 (OH), 1650 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=2.70 (1H, dd, *J*=6, 13 Hz), 3.02 (1H, dd, *J*=6, 13 Hz), 3.60 (1H, br-s), 4.7—5.4 (3H, m), 7.4—8.2 (4H, m). The hydroxyl group of compound **7c** was acetylated by acetic anhydride and *N,N*-dimethylaniline and the structure was confirmed.

4-Acetoxy-4-allyl-2,3-dibromo-1(4*H*)-naphthalenone (14c): White crystals from hexane–chloroform; mp 90—92 °C. MS; *m/z* 398, 400, 402 (M^+). Found: C, 45.24; H, 3.10; Br, 39.80%. Calcd for $C_{15}H_{12}O_3Br_2$: C, 45.03; H, 3.02; Br, 39.95%. IR (KBr); 1730 (C=O), 1640 (C=O) cm^{-1}. ^{1}H NMR (CCl_4) δ=2.10 (3H, s), 2.68 (1H, dd, *J*=6, 13 Hz), 3.05 (1H, dd, *J*=6, 13 Hz), 4.8—5.2 (3H, m), 7.3—7.7 (3H, m), 8.18 (1H, m).

4-Allyl-2,3-dichloro-4-hydroxy-1(4*H*)-naphthalenone (7d): White crystals from hexane–chloroform; mp 86—88 °C. MS; *m/z* 269, 271, 273 ($M+1^+$). Found: C, 58.02; H, 3.66; Cl, 26.14%. Calcd for $C_{13}H_{10}O_2Cl_2$: C, 58.02; H, 3.75; Cl, 26.35%. IR (KBr); 3440 (OH), 1640 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=2.78 (1H, dd, *J*=6, 14 Hz), 3.04 (1H, dd, *J*=6, 14 Hz), 3.48 (1H, br-s), 4.7—5.4 (3H, m), 7.4—8.2 (4H, m).

4-Allyl-4-hydroxy-1(4*H*)-naphthalenone (7f): Pale green oil. High-resolution mass spectrum. Found: *m/z* 200.0832. Calcd for $C_{13}H_{12}O_2$: M, 200.0837. IR (NaCl); 3400 (OH), 1660 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=2.61 (2H, d, *J*=8 Hz), 4.25 (1H, br-s), 4.7—5.6 (3H, m), 6.21 (1H, d, *J*=10 Hz), 6.91 (1H, d, *J*=10 Hz), 7.2—8.3 (4H, m).

4-Allyl-4-hydroxy-2-methyl-1(4*H*)-naphthalenone (7g): Colorless oil. High-resolution mass spectrum. Found: *m/z* 214.0990. Calcd for $C_{14}H_{14}O_2$: M, 214.0994. IR (NaCl); 3440 (OH), 1680 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=1.92 (3H, s), 2.62 (2H, m), 2.82 (1H, br-s), 4.94 (2H, m), 5.37 (1H, m), 6.70 (1H, s), 7.3—8.0 (4H, m). ^{13}C NMR ($CDCl_3$) δ=15.7, 47.9, 70.2, 119.6, 126.0, 126.3, 127.8, 129.9 (C_2), 131.3, 132.6, 134.6, 146.0, 147.1 (C_3), 185.0.

4-Allyl-4-hydroxy-3-methoxy-1(4*H*)-naphthalenone (7h): ^{13}C NMR ($CDCl_3$) δ=47.8 (t), 55.9 (q), 72.6 (s), 101.8 (d), 119.1 (t), 125.3 (d), 125.5 (d), 127.7 (d), 129.8 (s), 130.6 (d), 132.5 (d), 143.0 (s), 174.4 (s), 185.0 (s).

2,3-Dichloro-4-(3-methyl-2-butenyloxy)-1-naphthol (9b): Colorless oil. MS; *m/z* 296, 298, 300 (M^+). IR (NaCl); 3400 (OH), 1660 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=1.70 (3H, s), 1.80 (3H, s), 5.60 (1H, m), 5.86 (1H, s), 7.3—7.6 (2H, m), 7.9—8.2 (2H, m). The hydroxyl group of compound **9b** was acetylated as in the case of **7c** and the structure was confirmed.

1-Acetoxy-2,3-dichloro-4-(3-methyl-2-butenyloxy)naphthalene (15b): Yellow crystals from hexane–chloroform; mp 70—72 °C. MS; *m/z* 338, 340, 342 (M^+). Found: C, 59.90; H, 4.66; Cl, 20.63%. Calcd for $C_{17}H_{16}O_3Cl_2$: C, 60.19; H, 4.75; Cl, 20.90%. IR (KBr); 1740 (C=O) cm^{-1}. ^{1}H NMR (CCl_4) δ=1.70 (3H, s), 1.80 (3H, s), 2.45 (3H, s), 4.64 (2H, d, *J*=7 Hz), 5.67 (1H, t, *J*=7 Hz), 7.4—7.8 (3H, m), 8.0—8.2 (1H, m).

4-Benzyloxy-2,3-dichloro-1-naphthol (9c): White crystals from hexane–chloroform; mp 142—144 °C. MS; *m/z* 318, 320, 322 (M^+). Found: C, 63.97; H, 3.79; Cl, 22.21%. Calcd for $C_{17}H_{12}O_2Cl_2$: C, 64.26; H, 4.02; Cl, 22.01%. IR (KBr); 3370 (OH) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=5.15 (2H, s), 6.15 (1H, br-s), 7.3—8.4 (9H, m).

2-Chloro-3-(3-methyl-2-butenyl)-1,4-naphthoquinone (10b): Yellow plates from hexane–chloroform; mp 81—83 °C. MS; *m/z* 260, 262 (M^+). Found: C, 68.98; H, 4.93; Cl, 13.78%. Calcd for $C_{15}H_{13}O_2Cl$: C, 69.10; H, 5.03; Cl, 13.60%. IR (KBr); 1660 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=1.67 (3H, s), 1.80 (3H, s), 3.49 (2H, d, *J*=8 Hz), 5.09 (1H, m), 7.5—7.8 (2H, m), 7.9—8.2 (2H, m).

2-Benzyloxy-3-chloro-1,4-naphthoquinone (10c): Yellow crystals from hexane–chloroform; mp 120—122 °C. High-resolution mass spectrum. Found: *m/z* 282.0442. Calcd for $C_{17}H_{11}O_2{}^{35}Cl$: M, 282.0447. Found: *m/z* 284.0414. Calcd for $C_{17}H_{11}O_2{}^{37}Cl$: M, 284.0417. IR (KBr); 1670 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=4.15 (2H, s), 6.9—8.3 (9H, m).

2,3-Dichloro-4-hydroxy-4-(3-methyl-2-butenyl)-1(4*H*)-naph-

thalenone (11b): Colorless oil. MS; m/z 296, 298, 300 (M^+). IR (NaCl); 3420 (OH), 1650 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$) δ=1.21 (3H, s), 1.43 (3H, s), 2.60 (1H, dd, J=7, 12 Hz), 2.93 (1H, dd, J=7, 12 Hz), 3.87 (1H, br-s), 4.32 (1H, m), 7.2—8.1 (4H, m). The hydroxyl group of compound **11b** was acetylated as in the case of **7c** and the structure was confirmed.

4-Acetoxy-2,3-dichloro-4-(3-methyl-2-butenyl)-1(4*H*)-naphthalenone (16b): Colorless oil. MS; m/z 338, 340, 342 (M^+). Found: C, 60.06; H, 5.04; Cl, 20.61%. Calcd for $C_{17}H_{16}O_3Cl_2$: C, 60.19; H, 4.75; Cl, 20.90%. IR (NaCl); 1730 (C=O), 1650 (C=O) cm^{-1}. ^1H NMR (CCl_4) δ=1.23 (3H, s), 1.49 (3H, s), 2.08 (3H, s), 2.65 (1H, dd, J=14, 8 Hz), 2.99 (1H, dd, J=14, 8 Hz), 4.33 (1H, t, J=8 Hz), 7.3—7.7 (3H, m), 8.13 (1H, d, J=6 Hz).

4-Benzyl-2,3-dichloro-4-hydroxy-1(4*H*)-naphthalenone (11c): Colorless oil. MS; m/z 318, 320, 322 (M^+). IR (NaCl); 3420 (OH), 1670 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$) δ=3.12 (1H, d, J=13 Hz), 3.43 (1H, d, J=13 Hz), 3.96 (1H, br-s), 6.3—6.5 (2H, m), 6.9—8.0 (7H, m). The hydroxyl group of compound **11c** was acetylated as in the case of **7c** and the structure was confirmed.

4-Acetoxy-4-benzyl-2,3-dichloro-1(4*H*)-naphthalenone (16c): Colorless oil. MS; m/z 360, 362, 364 (M^+). Found: C, 63.17; H, 3.61; Cl, 19.55%. Calcd for $C_{19}H_{14}O_3Cl_2$: C, 63.18; H, 3.91; Cl, 19.63%. IR (NaCl); 1740 (C=O), 1650 (C=O) cm^{-1}. ^1H NMR (CCl_4) δ=2.11 (3H, s), 3.22 (1H, d, J=12 Hz), 3.52 (1H, d, J=12 Hz), 6.3—6.5 (2H, m), 6.8—7.7 (6H, m), 7.91 (1H, d, J=6 Hz).

CIDNP Examinations. A typical CIDNP examination of the photochemical reaction was undertaken as follows: suitable amounts ($\approx 10^{-2}$ mol dm^{-3}) of quinone **1** and tin reagent **2** or silane reagent **13** were dissolved in benzene-d_6 or in acetonitrile-d_3 in a Pyrex NMR sample tube. The sample purged with argon for 2 min was irradiated at room temperature by a high-pressure Hg lamp through a glass filter (Toshiba UV-35) and the ^1H NMR signals were observed before, during, and after irradiation.

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19) Regioselective formation of allyl quinol **7h** was also observed in the thermal reaction of allylstannane in the presence of BF_3,[15] while reverse regioselective formation for **7g** was observed in the thermal reaction of allylsilane in the presence of $TiCl_4$.[14]

20) Similar exclusive formation of α adducts in the thermal reaction of **1h** with **2b** in the presence of BF_3 was observed.[15]

21) Electron transfer from **2a** to triplet quinone **1d** generates an ion pair in the triplet state (μ>0). g-Factor of allyl radical (g=2.0026) is lower than that of the quinone anion radical ($g\approx$2.004-5; Δg<0). The products are generated by recombination of the radical ion (ε>0) or escape (ε<0). The sign of hyperfine coupling constant are calculated by McLachlan-Hückel MO and McConnell relationship. For example, Γne(-$\underline{C}H_2$-CH=CH_2)=$\mu\cdot\Delta g\cdot\varepsilon\cdot a$=+·−·+·−=+ for **5d** and Γne(-$\underline{C}H_2$-CH=CH_2)=+·−·−·−=− for **12a**. See, R. Kaptein, *J. Chem. Soc., Chem. Commun.*, **1971**, 732.

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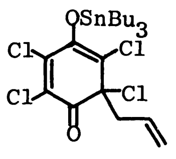

Fig. 4.

(1981).

31) It is said that $S_1 \rightarrow T_1$ process of quinones occurs with high efficiency (0.8—1.0),[16b)] and no fluorescence spectra of quinones **1** were observed. Thus, this reaction proceeds via triplet state.

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