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Photoallylation of Quinones with Allylstannane

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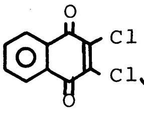
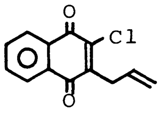
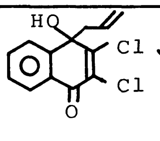
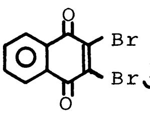
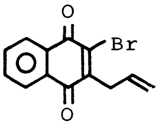
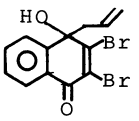
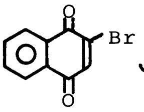
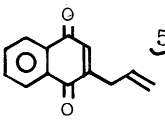
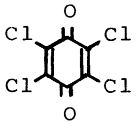
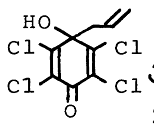
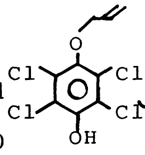
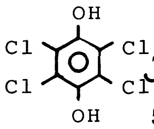
Photochemical reactions of halogeno-quinones with allylstannane in a benzene or an acetonitrile solution afforded allylated quinones and allyl quinols as major products. Nuclear spin polarization effects observed during irradiation support a contribution of electron transfer process.

Photochemistry of quinones with olefins1) as well as thermal allylation of quinones with allylstannanes in the presence of Lewis acid2) has been studied in our laboratory. It has been shown that reactions of the radical species generated by photo-induced electron transfer are synthetically useful.3,4) Although extensive photochemical reactions of allylic silanes have been published,3,5) there are few reports on the photochemical reactions of allylic stannanes.6) In this paper we describe the photoallylation of quinones with allylstannane including the reaction mechanism supported by the CIDNP technique.

Irradiation of a benzene solution containing 2,3-dichloro-1,4-naphthoquinone (1a, 1 mmol) and allyltri-n-butylstannane (2, 2 mmol) with a high pressure mercury lamp through a Pyrex filter for 3 h under argon afforded 2-allyl-3-chloro-1,4-naphthoquinone (3a, 35%) and 1-allyl-2,3-benzo-5,6-dichloro-1-hydroxycyclohex-5-en-4-one (4a, 15%) (Table 1, Run 1). Similarly, 3a (12%) and 4a (26%) were obtained in an acetonitrile solution (Run 2). The structures of the products were assigned from their spectral data,7) elemental analyses and chemical transformation.[8)] The results of photochemical reactions of quinones 1a-d with 2 are summarized in Table 1. The photochemical allylation proceeded at either quinone carbonyl carbon or halogenated ipso quinone ring position. Regioselectivities were low in both benzene and acetonitrile.

Table 1. Photochemical Reactions between Quinones and Allylstannane [a)]

Run	Quinones		Solvent	Products/ %[b)]						Conversion/ %
1		1a	C_6H_6	 3a	35	 4a	15			74
2	1a		CH_3CN	3a	12	4a	26			100
3		1b	C_6H_6	 3b	29	 4b	28			75
4	1b		CH_3CN	3b	47	4b	32			66
5		1c	C_6H_6	3b	20	 5c	9			81
6	1c		CH_3CN	3b	15	5c	15			97
7		1d	C_6H_6	 4d	20	 6d	20	 7d	50	100
8	1d		CH_3CN	4d	14	6d	28	7d	12	100

a) Irradiated for 3 h except Run 2 (35 h).

b) Isolated yield based on a starting quinone consumed.

To clarify the reaction mechanism, we have applied ^1H-CIDNP method. Irradiation of deaerated benzene-d_6 or acetonitrile-d_3 solution of quinone 1a ($\approx 10^{-2}$ mol dm^{-3}) containing allylstannane 2 ($\approx 10^{-2}$ mol dm^{-3}) gave rise to the strong nuclear spin polarization effects for the adducts 3a and the by-product, 1,5-hexadiene 8, whose assignments were indicated by arrows (Fig. 1).

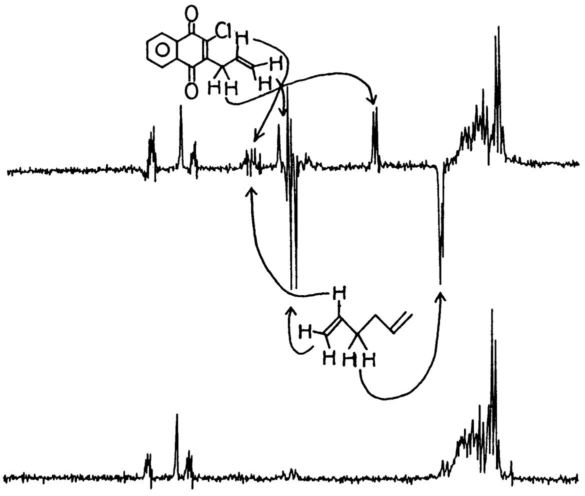
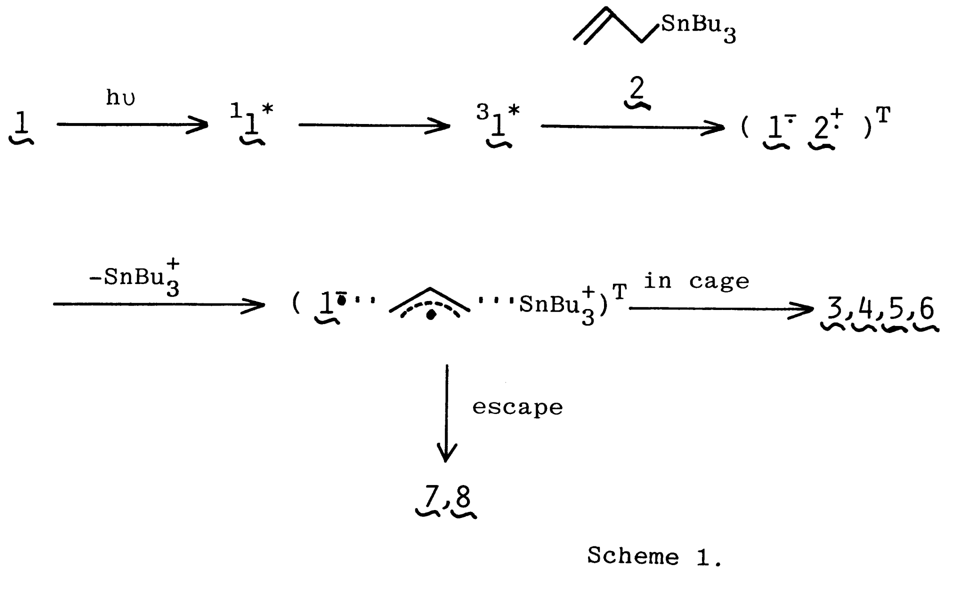


Fig. 1. ^{1}H NMR spectra (100MHz) of a benzene-d_6 solution containing 1a and 2 in the dark and (bottom) and during irradiation (top).

These polarizations are explained reasonably by Kaptein's rule9) and the reaction scheme is proposed as follows (Scheme 1). Because of the strong oxidizing power of these halogenated quinones, which is enhanced by photoexcitation, electron transfer occurs from donor 2 to the excited triplet quinone 1 and ion radical pair ($1^{\overline{\cdot}}$ $2^{+\cdot}$) is produced. Owing to the instability of $2^{+\cdot}$ 10) allyl radical may be generated from cleavage of the cation radical, forming subsequently ion radical pair ($1^{\overline{\cdot}}$, $CH_2=CH-CH_2^{\cdot}$, $SnBu_3^{+}$). The attack of allyl radical toward quinone anion radical $1^{\overline{\cdot}}$ gives the anionic intermediates, which afford the adducts 3, 4, 5, and 6. Quinone anion radical $1^{\overline{\cdot}}$ and allyl radical escaped from the cage would give rise to the reduction product 7 and the coupled product 8, respectively.



Scheme 1.

References

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6) R.M.Borg and P.S.Mariano, Tetrahedron Lett., 27, 2821 (1986); K.Mizuno, S.Toda, M.Ikeda, and Y.Otsuji, 52nd National Meeting of the Chemical Society of Japan, Kyoto, April 1986, Abstr., No. 4Z01.

7) Compound 3a: IR (KBr) 1675cm^{-1} (C=O); MS m/z 232 and 234 (M$^+$); ^{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), and 8.23 (2H, m). Compound 3b: IR (KBr) 1665cm^{-1} (C=O); MS m/z 276 and 278 (M$^+$); ^{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), and 8.20 (2H, m). Compound 4a: IR (KBr) 3440 (OH) and 1640 cm^{-1} (C=O); MS m/z 269, 271, and 273 (M+1$^+$); ^{1}H NMR (CDCl$_3$) δ=2.78 (1H, dd, J=6 and 14 Hz), 3.04 (1H, dd, J=6 and 14 Hz), 3.48 (1H, br), 4.7-5.4 (3H, m), and 7.4-8.2 (4H, m). Compound 4b: IR (KBr) 3360 (OH) and 1650 cm^{-1} (C=O); MS m/z 356, 358, and 360 (M$^+$); ^{1}H NMR (CDCl$_3$) δ=2.70 (1H, dd, J=6 and 13 Hz), 3.02 (1H, dd, J=6 and 13 Hz), 3.60 (1H, br), 4.7-5.4 (3H, m), and 7.4-8.2 (4H, m). Compound 4d: IR (KBr) 3400 (OH) and 1665 cm^{-1} (C=O); MS m/z 286, 288, 290, 292, and 294 (M$^+$); ^{1}H NMR (CDCl$_3$) δ=2.97 (2H, d, J=6 Hz), 4.41 (1H, br), and 5.0-5.5 (3H, m). Compound 6d: IR (KBr) 3430 cm^{-1} (OH); MS m/z 286, 288, 290, 292, and 294 (M$^+$); ^{1}H NMR (CDCl$_3$) δ=4.53 (2H, d, J=6 Hz), 5.3-5.6 (2H, m), 6.01 (1H, br), and 5.9-6.4 (1H, m).

8) Compound 6d was synthesized independently by the thermal allylation of the corresponding hydroquinone with K$_2$CO$_3$ and allyl bromide and the structure was confirmed.

9) Electron transfer from 2 to triplet quinone 1 generates a ion radical pair in the triplet state ($\mu>0$). g-Factor of allyl radical (g=2.0026) is lower than that of the quinone anion radical (g>2.0040; $\Delta g<0$). The products are generated by recombination of the radical ion ($\varepsilon>0$) or escape ($\varepsilon<0$). The signs of hyperfine coupling constant are calculated by McLachlan-Hückel MO and McConnell relationship. See, R. Kaptein, J.Chem.Soc.,Chem.Commun., 1971, 732.

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