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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 olefins<sup>1)</sup> as well as thermal allylation of quinones with allylstannanes in the presence of Lewis acid<sup>2)</sup> 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.<sup>3,4)</sup> Although extensive photochemical reactions of allylic silanes have been published,<sup>3,5)</sup> there are few reports on the photochemical reactions of allylic stannanes.<sup>6)</sup> 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 (<u>1</u>a, 1 mmol) and allyltri-n-butylstannane (<u>2</u>, 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 (<u>3</u>a, 35%) and 1-allyl-2,3-benzo-5,6-dichloro-1hydroxycyclohex-5-en-4-one (<u>4</u>a, 15%) (Table 1, Run 1). Similarly, <u>3</u>a (12%) and <u>4</u>a (26%) were obtained in an acetonitrile solution (Run 2). The structures of the products were assigned from their spectral data,<sup>7)</sup> elemental analyses and chemical transformation.<sup>8)</sup> The results of photochemical reactions of quinones <u>la-d with 2</u> 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.

							a )
Fable 1.	Photochemical	Reactions	between	Quinones	and	Allylstannane	а)

Run	Quinones	Solvent	Products/ % <sup>b)</sup>	Conversion/ %
1		с <sub>6</sub> н <sub>6</sub>	$\bigcirc \bigcirc $	ta 5 74
2	la	CH3CN	.3a 12 <u>4</u> a 2	26 100
3	Out Br Lb	<sup>с</sup> 6 <sup>н</sup> 6	$\bigcirc \bigcirc $	20 75 28
4	1b	CH <sub>3</sub> CN	<u>3</u> b 47 <u>4</u> b 3	66
5	O Br 1c	с <sub>6</sub> н <sub>6</sub>	3b 20 0 5	9 81
6	1c	CH3CN	<u>3</u> b 15 <u>5</u> c 1	.5 97
7	$\bigcup_{c_1}^{c_1} \bigcup_{c_2}^{0} \bigcup_{c_1}^{c_1} \underbrace{1d}_{0}$	с: С <sub>6</sub> н <sub>6</sub> с:	$ \begin{array}{c} \begin{array}{c} \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \begin{array}{c} \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} $	$\begin{array}{c} c_{1}^{c_{1}} \\ c_{1}^{c_{1}} \\ 50 \end{array}$
8	ld	CH <sub>3</sub> CN	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 <sup>1</sup>H-CIDNP method. Irradiation of deaerated benzene-d<sub>6</sub> or acetonitrile-d<sub>3</sub> solution of quinone <u>1</u>a  $(\approx 10^{-2} \text{mol dm}^{-3})$  containing allylstannane <u>2</u>  $(\approx 10^{-2} \text{mol dm}^{-3})$  gave rise to the strong nuclear spin polarization effects for the adducts <u>3</u>a and the by-product, 1,5-hexadiene <u>8</u>, whose assignments were indicated by arrows (Fig. 1).

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Fig. 1. <sup>1</sup>H NMR spectra (100MHz) of a benzene-d<sub>6</sub> solution containing <u>1</u>a and <u>2</u> in the dark and (bottom) and during irradiation (top).

These polarizations are explained reasonably by Kaptein's rule<sup>9)</sup> 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 ( $\underline{1}^{\cdot}, \underline{2}^{\dagger}$ ) is produced. Owing to the instability of  $\underline{2}^{\dagger}, \underline{10}$ ) allyl radical may be generated from cleavage of the cation radical, forming subsequently ion radical pair ( $1^{\cdot}$ ,  $CH_2=CH-CH_2^{\cdot}$ ,  $SnBu_3^{\dagger}$ ). The attack of allyl radical toward quinone anion radical  $\underline{1}^{\cdot}$  gives the anionic intermediates, which afford the adducts 3, 4, 5, and 6. Quinone anion radical  $\underline{1}^{\cdot}$  and allyl radical escaped from the cage would give rise to the reduction product 7 and the coupled product 8, respectively.



Scheme 1.

References 1) K.Maruyama, T.Otsuki, and S.Tai, J.Org.Chem., 50, 52 (1985); K.Maruyama, S.Tai, and H.Imahori, Bull.Chem.Soc.Jpn., 59, 1777 (1986). 2) Y.Naruta, J.Am.Chem.Soc., <u>102</u>, 3774 (1980). 3) P.S.Mariano, Acc.Chem.Res., 16, 130 (1983); K.Mizuno, M.Ikeda, and Y.Otsuji, Tetrahedron Lett., 26, 461 (1985). 4) T.Y.Liang and G.B.Schuster, J.Am.Chem.Soc., <u>108</u>, 546 (1986). 5) M.Ochiai, M.Arimoto, and E.Fujita, J.Chem.Soc., Chem.Commun., 1981, 460. 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 <u>3</u>a: IR (KBr)  $1675 \text{cm}^{-1}$  (C=O); MS m/z 232 and 234 (M<sup>+</sup>); <sup>1</sup>H NMR (CDCl<sub>2</sub>)  $\delta$ =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<sup>-1</sup> (C=O); MS m/z 276 and 278 (M<sup>+</sup>); <sup>1</sup>H NMR  $(CDC1_3)$   $\delta=3.66$  (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 <u>4</u>a: IR (KBr) 3440 (OH) and 1640 cm<sup>-1</sup> (C=O); MS m/z 269, 271, and 273 (M+1<sup>+</sup>); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ =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<sup>-1</sup> (C=O); MS m/z 356, 358, and 360  $(M^+)$ ; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ =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 <u>4</u>d: IR (KBr) 3400 (OH) and 1665 cm<sup>-1</sup> (C=O); MS m/z 286, 288, 290, 292, and 294 (M<sup>+</sup>); <sup>1</sup>H NMR  $(CDCl_3)$   $\delta=2.97$  (2H, d, J=6 Hz), 4.41 (1H, br), and 5.0-5.5 (3H, m). Compound 6d: IR (KBr) 3430 cm<sup>-1</sup> (OH); MS m/z 286, 288, 290, 292, and 294 (M<sup>+</sup>); <sup>1</sup>H NMR  $(CDCl_3)$   $\delta=4.53$  (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  $K_2CO_3$  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 ( $\epsilon$ >0) or escape ( $\epsilon$ <0). The signs of hyperfine coupling constant are calculated by McLachlan-Hückel MO and McConnell relationship. See, R. Kaptein, J.Chem.Soc.,Chem.Commun., <u>1971</u>, 732. 10) J.K.Kochi, "Organometallic Mechanisms and Catalysis," Academic Press, New York (1980).

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