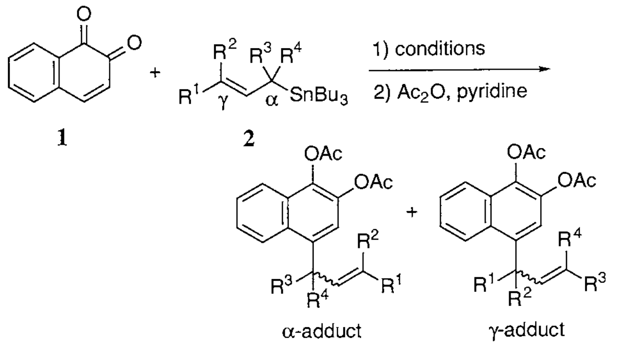
Contrasting Regiochemistry in Thermal and Photochemical Allylstannations of 1,2-Naphthoquinone

Yutaka Nishigaichi,* Naofumi Yoshida, Mikiya Matsuura, and Akio Takuwa
Department of Chemistry, Faculty of Science, Shimane University, 1060 Nishikawatsu-cho, Matsue, Shimane 690-8504

(Received May 10, 1999; CL-990374)

1,2-Naphthoquinone with γ-substituted allyltin reagents undergoes both thermal and photochemical reactions, which show the opposite regioselectivities to each other. The both reactions are supposed to proceed via the initial 1,2-addition, which occurs at the γ-position of the allyltin in the thermal reaction and at the less hindered α-position in the photoreaction, followed by the [3,3] allylic migration.

Quinones are known as an important class of compounds in biological, mechanistic, and synthetic fields.[1] Thus, a lot of reactions have been developed with *p*-quinones including allylstannation.[2] On the other hand, little has been dealt with *o*-quinones, which are also naturally occurring and of considerable interest. Actually, there are limited number of reports on their nucleophilic alkylation reaction which must be a key step for the synthetic conversion of a simple quinone toward the goal. Among such reactions, Lewis acid-promoted allylstannation is most successful.[3-5] Even less investigations have been done on their thermal and photochemical allylstannations in the absence of Lewis acids.[5,6] Herein, we will report that thermal and photochemical allylstannations of 1,2-naphthoquinone (**1**) (Scheme 1) proceed efficiently without any additives and they exhibit sharp contrast to each other in regiochemistry of the introduced allyl moiety.



Scheme 1.

First, **1** was treated with various allyltins (**2**) without any additives in CH_2Cl_2 or benzene (Table 1).[7] Unlike *p*-quinones, 1,4-addition products were isolated after acetylation. This seems to be one of a few examples of allyltrialkyltins reacting thermally toward a neutral species. Interestingly, the thermal reaction showed complete regiospecificity as summarized in Table 1. In every case attempted, the α-selectivity was observed, which is higher than that of the Lewis acid-mediated reaction.[3] When α-substituted allyltins were employed, sterically more congested regioisomers (branched adducts) were formed (entries 6-8). Even a tertiary substituent could be introduced (entry 8).

Table 1. Thermal reaction between 1,2-naphthoquinone (**1**) and allyltin reagents (**2**)

Entry	Allyltin reagent (2)				Conditions[a]	Product	Total
	R^1	R^2	R^3	R^4	(time/h)	ratio (α/γ)	yield/%
1	H	H	H	H	C (3)	-	31
2	Me	H	H	H	B (3)	100/0	71
3[b]	Vi[c]	H	H	H	A (2)	100/0	71
4	Ph	H	H	H	A (2)	100/0	99
5	Me	Me	H	H	A (5)	100/0	77
6[d]	H	H	Me	H	A (8)	100/0	54
7[d]	H	H	Ph	H	A (5)	100/0	40
8[d]	H	H	Me	Me	A (7)	100/0	38

[a]Conditions. A: 20 °C in CH_2Cl_2. B: 40 °C in CH_2Cl_2. C: 80 °C in benzene. [b]Taken from Ref 5. [c]Vi = vinyl ($CH=CH_2$). [d]Corresponding triphenyltin reagent was employed.

Next, the photoreaction between **1** and **2**, where the single electron transfer (SET) was expected from their redox potentials,[8] was attempted at the low temperature[9] to eliminate the facile thermal background reaction. The products were also isolated after acetylation. Again, the 1,4-adducts were obtained in moderate to good yields (Table 2).

Table 2. Photoreaction between **1** and **2**[a]

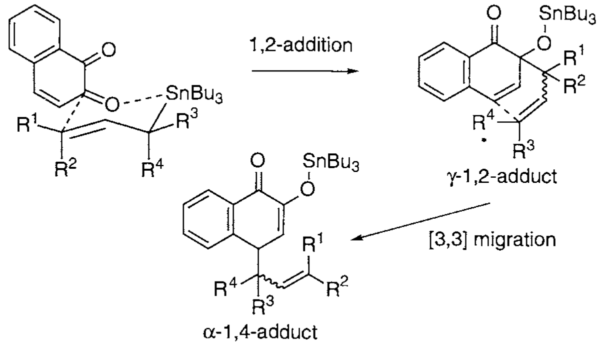
Entry	Allyltin reagent (2)				Product	Total
	R^1	R^2	R^3	R^4	ratio (α/γ)	yield/%
1	H	H	H	H	-	60
2	Me	H	H	H	39/61	74
3	Vi	H	H	H	29/71	80
4	Ph	H	H	H	15/85	71
5	Me	Me	H	H	25/75	58
6[b]	H	H	Ph	H	85/15	52
7[b]	H	H	Me	Me	80/20	31

[a]Conditions: see Ref 9. [b]Corresponding triphenyltin reagent was employed.

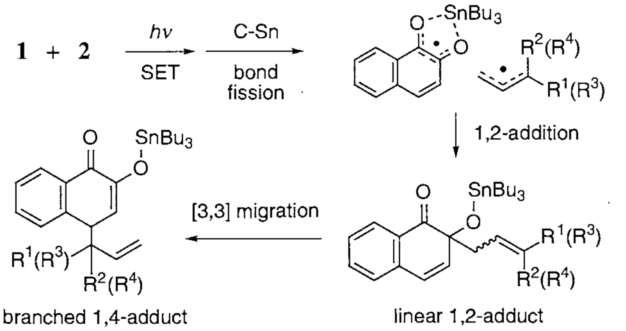
The point noteworthy is that the regioselectivity is opposite to that of the thermal reaction in entries 2-5. The γ-adducts, the more congested branched allylic regioisomers, were selectively produced from γ-substituted allyltins. This means the promoting method, heat or light, can control the regioselectivity. When α-substituted reagents were employed (entries 6, 7), the α-adducts were obtained selectively. In these instances, the α-adduct is the more congested branched isomer which corresponds to the γ-adduct in entries 4 and 5, indicating the photoreaction is not regiospecific but just regioselective.

The regio-reversal in thermal and photochemical reactions has been already reported in the acridinium ion-allyltin system,[10] but their regioselectivities are opposed to the present case. In addition, it is generally accepted that the thermal addition reaction of γ-substituted allyltins affords γ-adducts via the S_E2' mechanism,[11] whereas less congested linear adducts (α-adducts from γ-substituted allyltins) are preferred in the photoinduced reactions of iminium[10,12] and carbonyl[4,13] compounds including α-keto carbonyl compounds via the SET mechanism. Therefore, the present regioselectivities are most reasonably explained by the two-step process of the initial allylstannation and the subsequent allylic migration. The former would proceed via the 6-membered cyclic transition state in the thermal reaction (Scheme 2) or via the radical coupling after the SET in the photoreaction (Scheme 3), then the thermal [3,3] migration[14] would follow the each process, considering the previous report.[5]

The radical coupling in the photoreaction was rationalized by the fact that the α-substituted allyltins showed the similar regioselectivity of the branched adduct (entries 6, 7) to that from the corresponding γ-substituted allyltins (entries 4, 5). The regiochemistry was determined after the C–Sn bond fission, being sharp contrast to the thermal reaction.



Scheme 2.

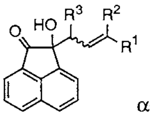


Scheme 3.

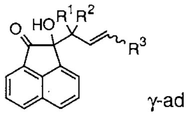
Table 3. Thermal and photochemical reactions between acenaphthenequinone and **2**

Allyltin reagent (**2**)				Product ratio (α/γ) (Total yield/%)	
R^1	R^2	R^3	R^4	therm.	photo.[c]
Me	H	H	H	0/100 (83)[a]	57/43 (86)
Vi	H	H	H	18/82 (78)[b]	80/20 (88)
Ph	H	H	H	0/100 (93)[b]	61/39 (91)
Me	Me	H	H	-	68/32 (71)
H	H	Ph	H	0/100 (84)[a, d]	42/58 (76)[d]

[a] 80 °C, 15 h, C_6H_6. [b] 20 °C, 48 h, CH_3CN. [c] >430 nm, 20 °C, 3 h, CH_3CN. [d] Corresponding triphenyltin reagent was employed.



α-adduct



γ-adduct

Such schemes are entirely consistent to the regiochemical preference in the reaction of acenaphthenequinone with various allyltins, which gave only 1,2-adducts (Table 3). The thermal reaction gave the γ-adducts predominantly, while the photoreaction preferred the linear adducts with almost the same product ratio from both γ- and α-substituted allyltins. These results indicate close similarity to the reported regioselectivities.[10]

After all, the regioselective thermal and photochemical reactions between 1,2-naphthoquinone and allyltins were found to proceed without any additives to give preferentially the α-1,4-adduct and the γ-1,4-adduct, respectively, from γ-substituted allyltins. This contrasting regiochemistry should be owing to the difference of the mechanisms. These reactions would be useful for organic synthesis because of no exposure of the labile quinone to a Lewis acid and the high regioselectivity especially for the thermal reaction.

References and Notes

1 "The Chemistry of the Quinonoid Compounds," ed by S. Patai and Z. Rappoport, Wiley, New York (1988). "Naturally Occuring Quinones, 4th ed," ed by R. Thomson, Chapman & Hall, New York (1996).

2 K. Maruyama, H. Imahori, A. Osuka, A. Takuwa, and H. Tagawa, *Chem. Lett.*, **1986**, 1719. K. Maruyama and H. Imahori, *Bull. Chem. Soc. Jpn.*, **62**, 816 (1989). K. Maruyama and Y. Matano, *Bull. Chem. Soc. Jpn.*, **62**, 3877 (1989).

3 Y. Naruta, *J. Am. Chem. Soc.*, **102**, 3774 (1980). K. Maruyama, A. Takuwa, Y. Naruta, K. Satao, and O. Soga, *Chem. Lett.*, **1981**, 47. A. Takuwa, Y. Naruta, O. Soga, and K. Maruyama, *J. Org. Chem.*, **49**, 1857 (1984). A. Takuwa, O. Soga, T. Mishima, and K. Maruyama, *J. Org. Chem.*, **52**, 1261 (1987).

4 A. Takuwa, Y. Nishigaichi, K. Yamashita, and H. Iwamoto, *Chem. Lett.*, **1990**, 639.

5 Y. Nishigaichi and A. Takuwa, *Chem. Lett.*, **1990**, 1575.

6 K. Maruyama and Y. Matano, *Chem. Express*, **5**, 133 (1990). K. Maruyama and Y. Matano, *Nippon Kagaku Kaishi*, **1989**, 1351.

7 A solution of **1** and **2** (1.2 equiv) was stirred under nitrogen under indicated conditions in Table 1. After the completion of the reaction, acetic anhydride and pyridine were added to the reaction mixture, which was stirred overnight at r.t. before the work-up.
Selected ^{1}H NMR data for the major product of entry 4, Table 1 (α-adduct): 3.95 (d, 2H, J = 5.6 Hz), 6.44-6.49 (m, 2H).

8 Allyltins: 0.42-1.06 V, **1**: -0.23 V (vs Ag/AgCl in CH_3CN).

9 An allyltin reagent (**2**) was added to the propionitrile solution of **1** cooled in a dry-ice/methanol bath and irradiated by a xenon lamp through a Toshiba VY-43 filter (>430 nm). After 3 h irradiation at -78 °C, the reaction was quenched with an aqueous $Na_2S_2O_4$ solution when still cold, then the mixture was warmed up to r.t. The crude product mixture was acetylated in CH_2Cl_2 as above.
Selected ^{1}H NMR data for the major product of entry 4, Table 2 (γ-adduct): 4.90 (dt, 1H, J = 17.1, 1.5 Hz), 5.29 (dt, 1H, J = 10.3, 1.5 Hz), 5.46 (d, 1H, J = 6.6 Hz), 6.36 (ddd, 1H, J = 16.9, 10.3, 6.6 Hz).

10 S. Fukuzumi, M. Fujita, and J. Otera, *J. Chem. Soc., Chem. Commun.*, **1993**, 1536.

11 Y. Yamamoto and N. Asao, *Chem. Rev.*, **93**, 2207 (1993).

12 K. Ohga and P. S. Mariano, *J. Am. Chem. Soc.*, **104**, 617 (1982). K. Ohga, U. C. Yoon, and P. S. Mariano, *J. Org. Chem.*, **49**, 213 (1984).

13 A. Takuwa, Y. Nishigaichi, K. Yamashita, and H. Iwamoto, *Chem. Lett.*, **1990**, 1761. A. Takuwa, Y. Nishigaichi, and H. Iwamoto, *Chem. Lett.*, **1991**, 1013. A. Takuwa, Y. Nishigaichi, T. Yamaoka, and K. Iihama, *J. Chem. Soc., Chem. Commun.*, **1991**, 1359. A. Takuwa, J. Shiigi, and Y. Nishigaichi, *Tetrahedron Lett.*, **34**, 3457 (1993).

14 B. Miller, *Acc. Chem. Res.*, **8**, 245 (1975). K. Krohn, *Synthesis*, **1997**, 1115.