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Reactions between Pentadienyltins and 1,2-Naphthoquinones. Regiocontrolled Introduction of Pentadienyl Group

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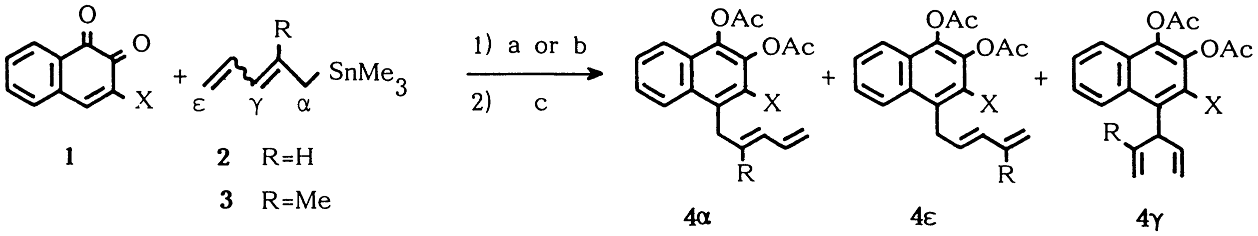
1,2-Naphthoquinones were efficiently pentadienylated at their 4-position with use of pentadienyltin (PDT) reagents. Regiochemistry of the introduced pentadienyl moiety, α, γ, or ε position of the PDT, was controlled by both the reaction conditions and the reactants.

Among various organotin compounds,$^{1)}$ 2,4-pentadienyltin (PDT) is regarded as a useful reagent introducing a conjugated pentadienyl chain into various electrophiles through the mediation of an appropriate Lewis acid.$^{2,3)}$ In particular, α,β-unsaturated carbonyl compounds can be successfully pentadienylated without formation of Diels-Alder adducts. Even strongly dienophilic 1,4-quinones can be also employed as suitable substrates affording 2,4-pentadienylhydroquinones.$^{2)}$ In contrast, pentadienylsilane preferencially gives Diels-Alder adducts.$^{3,4)}$

Unlike the reaction of 1,4-quinones, that of 1,2-quinones, which are also widespread compounds in nature,$^{5)}$ has not been paid much attention to so far. Therefore, the reaction of PDT with 1,2-quinones was examined in order to elucidate the extensive applicability of PDT and the reactivity of 1,2-quinones. We describe here that PDT can efficiently pentadienylate



a) Room temperature (for Table 1); b) (i-PrO)$_3$TiCl (3 equiv.), -78 °C (for Table 2); c) Ac$_2$O, pyridine.

Scheme 1.

Table 1. Thermal reaction between 1,2-NQs and PDTs[a)]

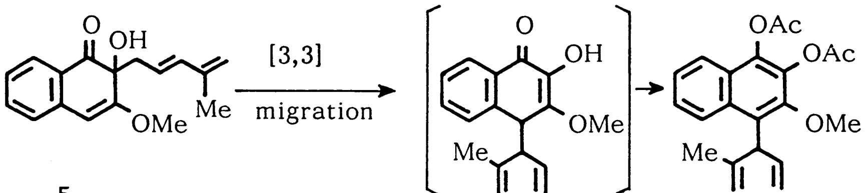
Entry	Quinone **1** (X)	PDT	Regioisomeric ratio of **4**[b)] **4** α	**4** ε	**4** γ	Total yield of **4** / %
1	**a** (OMe)	2	100		0	99
2	**b** (Me)		100		0	94
3	**c** (H)		100		0	71
4	**d** (Cl)		100		0	87
5	**e** (CO_2Me)		100		0	88
6	**a**	3	57	43	0	83
7	**b**		46	54	0	73
8	**c**		65	35	0	59
9	**d**		49	51	0	93
10	**e**		50	50	0	92

a) Conditions a in Scheme 1. b) Determined by ^{1}H NMR spectroscopy.

Table 2. Lewis acid mediated reaction between 1,2-NQs and PDTs[a)]

Entry	Quinone **1** (X)	PDT	Regioisomeric ratio of **4**[b)] **4** α	**4** ε	**4** γ	Total yield of **4** / %
1	**a** (OMe)	2	40		60	58
2	**b** (Me)		25		75	quant
3	**c** (H)		29		71	73
4	**d** (Cl)		38		62	88
5	**e** (CO_2Me)		88		12	89
6	**a**	3	0	0	100	61
7	**b**		10	10	80	78
8	**c**		0	0	100	70
9	**d**		8	13	79	85
10	**e**		10	78	12	74

a) Conditions b in Scheme 1. b) Determined by ^{1}H NMR spectroscopy.



5 **4γ**

(1)

various 1,2-naphthoquinones in two different regiochemical manners controlled by reaction conditions; thermal and Lewis acid-mediated reactions (Scheme 1).[6)]

In Table 1 are listed the results of the thermal reaction. Various 3-substituted 1,2-naphthoquinones (1,2-NQs; **1**) were allowed to react with 2,4-pentadienyltin (**2**; E/Z=8/2) in the absence of Lewis acid in CH_2Cl_2 under nitrogen (entries 1-5). The reactants were readily consumed at room temperature and the products were isolated in good to excellent yield[7)] after acetylation. The exclusive product was found to be 4-(2,4-pentadienyl)-1,2-diacetoxynaphthalenes (**4α** or **4ε**), which were the products pentadienylated at the terminal positions of the pentadienyl moiety. No pentadienylation at the internal γ-position was observed. Moreover, no Diels-Alder adduct was contaminated at all,[8)] while 1,4-NQs were found to readily give only Diels-Alder adducts under similar reaction conditions.[9)]

If the applied PDT has an unsymmetric pentadienyl moiety, regioselectivity (α or ε of PDT) comes to an issue. Though 2-methyl-2,4-pentadienyltin (**3**; E/Z=1/9) also reacted with 1,2-NQs in high yields under the same conditions, the regioselectivity was not observed; α-adduct (**4α**)/ε-adduct (**4ε**) was nearly 1/1 (entries 6-10). This fact implies that the C-Sn bond cleaved before the C-C bond formation.[10)]

As is well known, Lewis acid mediates the allylation of various 1,2-quinones by allyltin compounds.[6)] The results of similar reactions between **1** and PDTs are summarized in Table 2. In the case of PDT **2**, a branched pentadienyl group, i.e. 1,4-pentadien-3-yl group was preferentially introduced into the 4-position of 1,2-NQs (entries 1-4). When 2-methylpentadienyltin (**3**) was used, this γ-selectivity was increased much more (entries 6-9).

In the reaction with 3-methoxy-1,2-NQ (**1a**; entry 6), was also isolated 19% of 1,2-adduct **5** which was found to have a pentadienyl group introduced at ε-position of PDT **3**. When $BF_3 \cdot OEt_2$ was employed as a Lewis acid in this reaction, 1,2-addition exclusively proceeded to give **5**, which was then exposed to $(i\text{-PrO})_3TiCl$ to give the migrated γ-adduct in 54% yield.[11)] From these findings it is concluded that the characteristic γ-selectivity resulted from the initial 1,2-addition of PDT at its ε-position and the subsequent thermally allowed [3,3] sigmatropic migration (equation 1).

In contrast, when 1,2-NQ had an electron-withdrawing group at its 3-position, the reaction showed high ε-selectivity (entries 5 and 10), which is also contrast to that in the thermal reaction (entry 10 in Table 1). This can be rationalized by the direct 1,4-addition to the highly activated 4-position of **1e**, where the C-C bond began to form at the terminal ε-position of **3** before the completion of the C-Sn bond cleavage.

As mentioned above, it has been found that 1,2-NQs were efficiently pentadienylated in two regioselective manners, i.e. α/ε- and γ-selectively. It should be pointed out that this ambident selectivity can be controlled by the reaction conditions and the combination of the reactants. As well as the mechanistic aspects, the synthetic features here stir up our interest. The introduced dienyl moiety is such a reactive function that it will be a clue to further functionalization for synthesis of quinonoid compounds. Extended mechanistic and synthetic studies are now in progress.

References

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6) Allylation of 1,2-naphthoquinones using allyltins has already been reported. 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).

7) Thermal reaction of 1,2-NQ with allyltin also proceeded but at very low efficiency.

8) The lack of the reactivity of 1,2-NQs toward Diels-Alder reaction here is explainable as follows; (i) insufficient overlap of the orbitals between the reactants due to the small LUMO coefficient (HMO) at C-3 of 1,2-NQ and (ii) low reduction potential of 1,2-NQ which facilitates the electron transfer[10)] from PDT.

9) Diels-Alder reaction of PDTs will be described elsewhere.

10) This observation does not conflict with electron transfer mechanism proposed for the thermal reaction between quinones and allyltins. K. Maruyama and Y. Matano, Nippon Kagaku Kaishi, 1989, 1351; Bull. Chem. Soc. Jpn., 62, 3877 (1989).

11) Further reaction with $BF_3 \cdot OEt_2$ resulted in decomposition of **5**.

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