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A CONVENIENT ALLYLATION OF ORTHO-QUINONES. AN EXTENSION ON THE UTILITY OF ALLYLTIN REAGENTS

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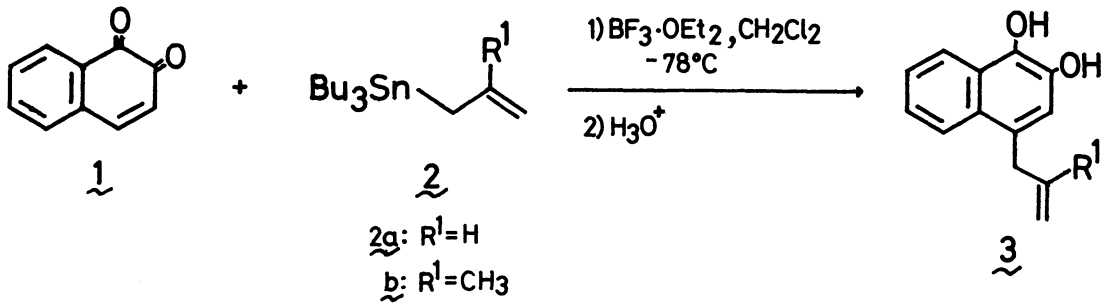
Lewis acid catalyzed allylation of 1,2-naphthoquinones and o-benzoquinones with allyltributyltins gave monoallylation products in reasonable to high yields.

Introduction of an isoprenoid functionality into a quinone ring is an essential problem in the synthesis of isoprenoid quinones which play a pivotal role in the electron transport chain in both photosynthetic and respiratory processes.[1] Several methods have been employed to synthesis of these biological active isoprenyl quinones.[2] However, these methods remains fundamentally limited by the aspects of yields, regio- and stereoselectivity, and the difficulty of preparing a starting materials. Recently, we reported the direct introduction of allyl or prenyl group into p-quinones using allyltin reagents overcomes such limitations.[3] Thus, coenzyme Q series, vitamin K series, and plastoquinone-1 were prepared satisfactorily by this method.[3),4] In addition, we revealed that the reaction appeared to proceed through allylquinol intermediates which underwent [1,2]rearrangement under influence of BF_3 to give allylhydroquinones.[4] Since little is known about the allylation of o-quinones, extension of this allylating method to o-quinones will open an important route to the synthesis of natural products.

We wish to report here the allylation of 1,2-naphthoquinone and o-benzoquinones with allyltributyltin reagent in the presence of BF_3OEt_2. Thus, the reaction of allyltributyltins[5] (2) with 1,2-naphthoquinones in dichloromethane gave allyl substituted 1,2-naphthalenediols (3) in fair to good yields (Scheme 1).

Typically the reaction was carried out by dropwise addition of an allyltributyltin (2) (0.6 mmol) to a stirred dichloromethane solution (10 ml) of quinone (1) (0.5 mmol) and BF_3OEt_2 (0.75 mmol) under nitrogen at -78°C. After the addition, the resulting mixture was stirred continuously and allowed to stand at



1 2 3

2a: R^1=H
b: R^1=CH_3

(Scheme 1)

room temperature. The reaction was quenched by addition of 2N-HCl and products were extracted with ether. Since 4-allyl-1,2-naphthalenediols (3) were very air-sensitive, the dried ethereal extract was quickly concentrated by evaporator *in vacuo*, and treated with acetic anhydride-pyridine under nitrogen or otherwise treated with silver oxide to give quinones. Thus obtained diacetates or quinones were purified by preparative thin layer chromatography on silica gel(developing solvent: benzene). The products and their isolated yields are summarized in Table 1.

Marked contrast of the present reaction compared with those reported[2] is exemplified in the allylation of 1,2-naphthoquinone. The reaction with π-2-methallylnickel bromide complexes gave 2 : 1 mixture of the mono-(49%) and diallylated(29%) products. By the present method monoallylated product was afforded exclusively.

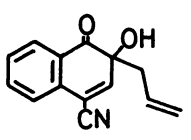
o-Benzoquinones also reacted with allyltributyltin to give the corresponding monoallylcatechols in very high yields (Table 1). Thus, o-benzoquinone, and its 4-methyl, and 4-*tert*-butyl derivatives produced the corresponding 5-allyl substituted catechols. In contrast, 3,5-dimethyl-o-benzoquinone afforded exclusively 4-allyl-3,5-dimethylcatechol. Remarkable thing is that halogen atoms and cyano group as the substituent on quinone ring are inert to this allylation.

To clarify the initial stage of the reaction of o-quinone with allyltin reagent, the reactions of 4-substituted 1,2-naphthoquinones and sterically hindered 3,5-di-*tert*-butyl-o-benzoquinone were examined. Thus, 4-cyano-1,2-naphthoquinone, 4-methoxy-1,2-naphthoquinone,[6] and 3,5-di-*tert*-butyl-o-benzoquinone gave the corresponding 1,2-addition products to carbonyl in high yields, i.e., 4, 5, and 6 given in Table 1. In the allylation of 4-cyano-1,2-naphthoquinone the 1,2-addition took place at 2-carbonyl, but in that of 4-methoxy-1,2-naphthoquinone at 1-carbonyl, probably because of the influence of the mesomeric effect of the substituents. Therefore, initial site of the allylation may be governed with electron density of carbonyl carbon at position 1 or 2 of quinone.

Table 1. Allylation of Ortho-quinones with Allyltributyltins

Quinone[a]	Allyltin	Product[b]	Yield[c] (%)
1,2-NQ	2a	4-Allyl-1,2-naphthalenediol	78[d]
	2b	4-(2-Methyl-2-propenyl)-1,2-naphthalenediol	78[d]
6-Bromo-1,2-NQ	2a	4-Allyl-6-bromo-1,2-naphthalenediol	68[d]
	2b	4-(2-Methyl-2-propenyl)-6-bromo-1,2-naphthalenediol	61[d]
3-Methoxy-1,2-NQ	2a	4-Allyl-3-methoxy-1,2-naphthalenediol	65[e]
	2b	3-Methoxy-4-(2-methyl-2-propenyl)-1,2-naphthalenediol	79[e]
3-Chloro-1,2-NQ	2b	3-Chloro-4-(2-methyl-2-propenyl)-1,2-naphthalenediol	89[e]
4-Cyano-1,2-NQ	2a	4	87
4-Methoxy-1,2-NQ	2a	5	91
o-BQ	2a	4-Allylcatechol	62
4-Methyl-o-BQ	2a	4-Allyl-5-methylcatechol	93
4-*tert*-Butyl-o-BQ	2a	4-Allyl-5-*tert*-butylcatechol	93[d]
3,5-Dimethyl-o-BQ	2a	4-Allyl-3,5-dimethylcatechol	85
3,5-di-*tert*-Butyl-o-BQ	2a	6	93

[a] 1,2-NQ: 1,2-Naphthoquinone; o-BQ: o-Benzoquinone. [b] Characterized by infrared and nmr spectra after acetylation or oxidation to quinone. [c] Yields refer to isolated products, based on used quinone. [d] Yields after acetylation with acetic anhydride-pyridine. [e] Yields after oxidation with silver oxide.



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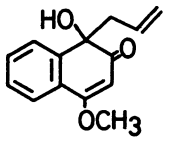

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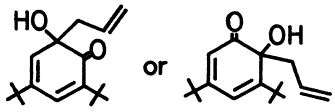

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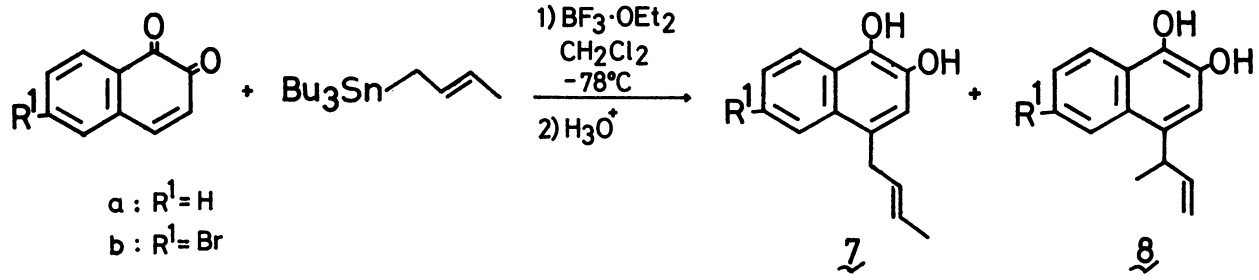
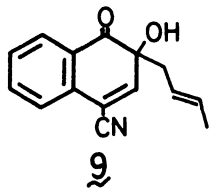
In addition, we examined the reaction of 1,2-naphthoquinones with unsymmetrical allylic reagent, i.e., 2-butenyltributyltin,[7] under the same reaction conditions (Scheme 2).



(Scheme 2)

When 4-cyano-1,2-naphthoquinone was treated with crotyltin reagent and quenched at -30°C, α-adduct (1,2-addition product) (9) was obtained exclusively (isolated yield: 91%). This indicates that addition of allyltin reagent to carbonyl of 1,2-naphthoquinone occurs at the α allyl terminus. However, 1,2-naphthoquinone and 6-bromo-1,2-naphthoquinone gave a mixture of rearranged products, 7 (α-adduct) and 8 (γ-adduct) as shown in scheme 2, and their distributions were shown in Table 2. This is a quite interesting difference compared with the results in the reactions of p-quinones,[4] but the due course of the reaction will be written in future.



9

Table 2. Reaction of 2-butenyltributyltin with 1,2-naphthoquinone[a]

Quinone	Product	Yield[b] (%)	Product distribution[c] (%)	
			α-adduct (7)	γ-adduct (8)
1,2-Naphthoquinone	7a and 8a	85	54	46
6-Bromo-1,2-naphthoquinone	7b and 8b	91	73	27

[a]Reactions were performed in 0.5 mmol scale under standard conditions.
[b]Isolated yield after acetylation, based on used quinone.
[c]Determined by ^{1}H-nmr.

References and Notes

1) R.M.Bentley and I.M.Campbell in "The Chemistry of Quinonoid Compounds", part 2, S.Patai, Ed., Wiley, New York, N.Y., 1974, pp 683-736.
2) For example, L.S.Hegedus, B.R.Evans, D.E.Korte, E.L.Watermann, and K.Sjöberg, J. Am. Chem. Soc., 98, 3901 (1976) and references cited theirin.
3) K.Maruyama and Y.Naruta, Chem. Lett., 1978, 431; Y.Naruta, ibid., 1979, 881; Y.Naruta, S.Ushida, and K.Maruyama, ibid, 1979, 919; K.Maruyama and Y.Naruta, J. Org. Chem., 43, 3796 (1978); Y.Naruta and K.Maruyama, Chem. Lett., 1979, 885.
4) Y.Naruta, J. Am. Chem. Soc., 102, 3774 (1980); Y.Naruta, J. Org. Chem., in press.
5) Allyltributyltin (2a) and 2-methyl-2-propenyltributyltin (2b) were prepared according to the literature: cf. E.A.Abel and R.J.Rowley, J. Organomet. Chem., 84, 199 (1975).
6) When 2 equiv. of BF_3OEt_2 to 4-methoxy-1,2-naphthoquinone was used, the reaction did not occur, and the quinone was recovered almost quantitatively, but use of 10 equiv. BF_3OEt_2 to the quinone accomplished the reaction to give 5.
7) 2-Butenyltributyltin was prepared from tributyltin lithium and 1-chloro-2-butene: cf. E.Matarasso-Tchiroukhine and P.Cadiot, J. Organomet. Chem., 121, 155 (1976) and Ref. (4).

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