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REACTION OF 2,3-DIHYDRO-2,3-EPOXY-1,4-NAPHTHOQUINONE WITH ALLYLTRIBUTYLTIN. DIRECT ALLYLATION OF EPOXYQUINONE NUCLEUS [1]

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2-Alkyl-2,3-dihydro-2,3-epoxy-1,4-naphthoquinone reacted with allyltributyltin and stereo- and regiospecific allylation of its carbonyl was attained giving 3-alkyl-1-allyl-2,3-epoxy-4-oxo-1,2,3,4-tetrahydro-1-naphthol.

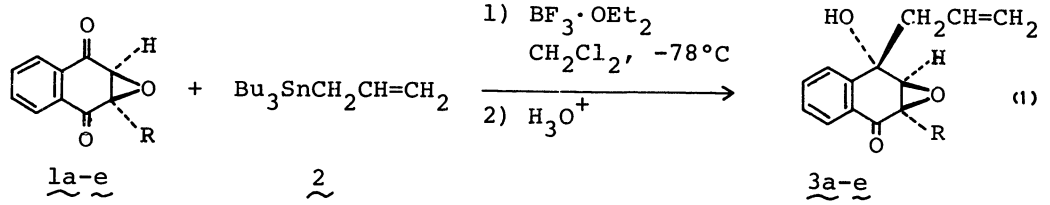
Epoxyquinone is an important intermediate in the synthesis of functionalized quinones, especially of naturally occurring hydroxyquinones and their derivatives.[2] Recently photochemical modifications of epoxynaphthoquinones were reported.[3,4]

It has been known that alkylation of α-epoxyketone with organometallic reagents (RLi or RMgX) occurred at carbonyl in preference to oxirane ring.[5] However, in the reaction with a variety of organometallic alkylating reagents (e.g. RLi, R_2CuLi, RCu and RMgX), epoxyquinone gave 2-hydroxy-1,4-naphthoquinone and/or unidentified complex mixture.[6] By our knowledge direct alkylation of epoxyquinone has never been accomplished.

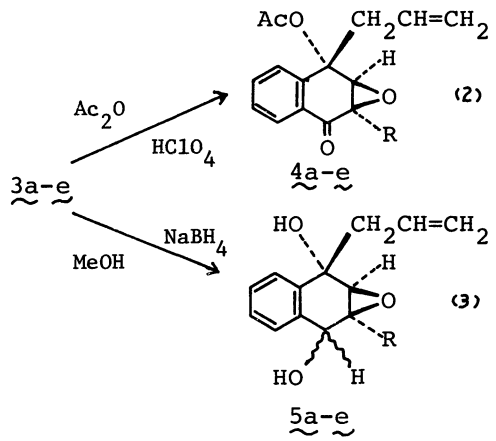
We wish to report here the regiospecific introduction of an allyl group to epoxyquinone nucleus using allyltin reagent.[7] The reaction was carried out by addition of an allyltin 2 (1 mmol) to a dichloromethane solution of 1a-e (1 mmol) in the presence of boron trifluoride etherate (1 mmol) under nitrogen at -78°C. After the addition was completed, the temperature of reacting mixture was gradually elevated to room temperature within an hour. The reaction was quenched by addition of 2N hydrochloric acid and the crude product was extracted by ether. The ethereal layer was usually worked-up, and the products were purified by preparative thin layer chromatography. Thus, 3a-e were isolated and their structures were confirmed by the subsequent acetylation (eq. 2) and hydride reduction (eq. 3).

From ^{1}H-NMR of 4 and 5, the stereochemistry and the position of alkyl substituent R were determined[8]. (i) In acetate 4a, one of the two methine absorptions down-field shifted ca. 1 ppm compared with that of the other. In 4b-e, the similar down-field shift of epoxymethine proton was observed without exception. The down-field shift can be explained in terms of the deshielding effect of ester carbonyl. (ii) Moreover, the epoxy methine proton of 5b-e showed no coupling with the C-4 methine proton (in 5a $J_{H(C-3)-H(C-4)}=2Hz$). (iii) The ^{13}C-NMR of 3a-e substantiated further the structure of the allylated products.

Thus, the allylation regio- and stereospecifically occurs at sterically less crowded carbonyl of epoxyquinone without scission of oxirane ring, and the allyl group



1a-e 2 3a-e



4a-e 5a-e

Epoxyquinone	Product[a]	% Yield[b]
1a, R= H	3a	84(96)
1b, CH_3	3b	93
1c, C_2H_5	3c	77
1d, n-C_3H_7	3d	80
1e, t-C_4H_9	3e	91

a) Satisfactory (1) spectroscopic, (2) mass spectroscopic, and/or analytical data were obtained for all products.
b) Yield in parenthesis determined by GLPC; all others are of purified products after isolation.

is situated in *cis* configuration to the oxirane ring.

So far as we examined, allyltin reagents are likely to be the one of the promising allylating reagents of carbonyl group with high chemoselectivity and their application and mechanistic study of this allylation are now under way.

References

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4) S.Arakawa, J. Org. Chem., 42, 3800 (1977)
5) N.H.Cromwell, J.L.Martin, J. Org. Chem., 33, 1890 (1968)
6) The reaction was carried out by addition of an organometallic reagent (1 mmol) in THF or ether to a solution of epoxyquinone 1a (1 mmol) at -78°C. n-BuLi, n-Bu_2CuLi and n-BuCu gave 2-hydroxy-1,4-naphthoquinone almost quantitatively. MeMgI gave an intractable mixture accompanied with a small amount of 2-hydroxy-1,4-naphthoquinone.
7) Insertion reactions of carbonyl groups(ketone or aldehyde) into Sn-C bond of allyltin compound without additives have been known. The reaction was limited to polarized carbonyls attached to electron withdrawing groups and needed higher reaction temperature. (a) K.König, W.P.Newmann, Tetrahedron Lett., 495 (1967) (b) C.Servans, M.Pereyre, J. Organomet. Chem., 26, C4 (1971); idem., ibid., 35, C20 (1972) (c) E.A.Abel,R.J.Rowley, ibid., 84, 199 (1975)
8) ^{1}H-NMR spectra (CCl_4): 3a: δ=2.42(dd,2H,J=2,7Hz), 3.46(d,1H,J=4Hz), 3.54(d,1H,J=4Hz), 3.8(bs,1H), 4.7-5.5(m,3H), 7.1-7.7(m,4H). 4a: δ=2.15(s,3H), 2.92(dq,2H,J=6,10Hz), 3.50(d,1H,J=4Hz), 4.56 (d,1H,J=4Hz), 4.7-5.2(m,3H), 7.40 and 7.70(m,4H). 5a: δ=2.41(d,2H,J=6Hz), 3.15(d,1H,J=4Hz), 3.37(dd,1H,J=2,4Hz), 3.4(bs,2H), 4.64(d,1H,J=2Hz), 4.7-5.6(m,3H), 7.2-7.6(m,4H). 3b: δ=1.59(s,3H), 2.48(bs,1H), 2.60(m,2H),3.56(s,1H), 4.8-5.5(m,3H), 7.3-7.9(m,4H). 4b: δ=1.54 (s,3H), 2.15(s,3H), 2.96(m,2H), 4.41(s,1H), 5.00(m,3H), 7.3-7.9(m,4H). 5b: δ=1.43(s,3H), 2.46 (d,2H,J=6Hz), 2.92(s,1H), 3.3(bs,2H), 4.50(s,1H), 4.7-5.4(m,3H), 7.2-7.6(m,4H).
The ^{1}H-NMR spectra of the other derivatives, 4c-e and 5c-e, were also compatible with their structures.

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