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Preliminary communication

The reaction of trialkylboranes with 1,4-naphthoquinone: a new, convenient synthesis of 2-alkyl-1,4-naphthalenediols. Evidence for a free-radical chain mechanism

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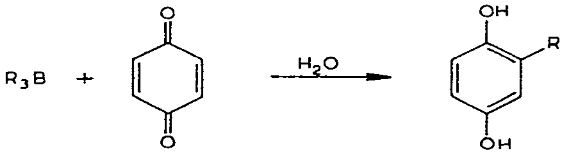
Trialkylboranes undergo a facile reaction with *p*-benzoquinone producing quantitative yields of the corresponding 2-alkylhydroquinones after hydrolysis[1, 2].



(1)

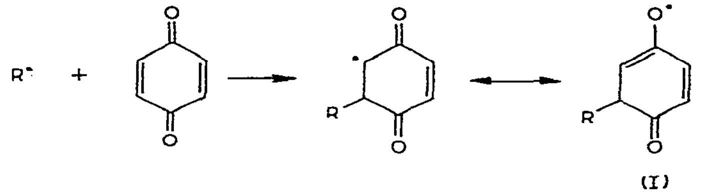
The reaction is readily applicable to a wide variety of trialkylboranes and is limited only by the fact that quinones other than *p*-benzoquinone are apparently unreactive.

It has been postulated[2b] that the reaction proceeds via a 'reductive alkylation,' *i.e.*, direct 1,2-addition of the trialkylborane to the carbonyl group followed by acid catalyzed migration of the alkyl group from the carbonyl carbon to the adjacent carbon.

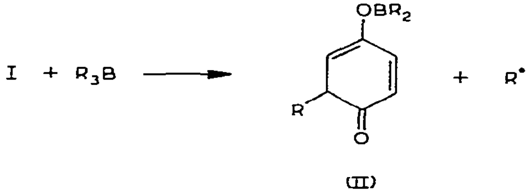
In light of current findings which demonstrate that the 1,4-addition of trialkylboranes to α,β-unsaturated carbonyl systems[3] is a free radical process, it appeared likely that the reaction of *p*-benzoquinone with trialkylboranes is also a free radical 1,4-addition reaction. This postulation gains further support from the fact that 1,2-addition of trialkylboranes to the carbonyl group is unknown except for certain 'active' organoboranes such as triallylborane[4].

The reaction can then be visualized as the addition of a free radical to the carbon-carbon double bond (Eqn. 2), producing a free radical intermediate, I. In the presence of free trialkylborane, this intermediate (I) reacts through the oxygen atom to form the enol borinate, II, with its very strong boron-oxygen bond (Eqn. 3). The enol borinate then hydrolyzes to form the unstable enol, III, which readily tautomerizes to the observed product, IV.

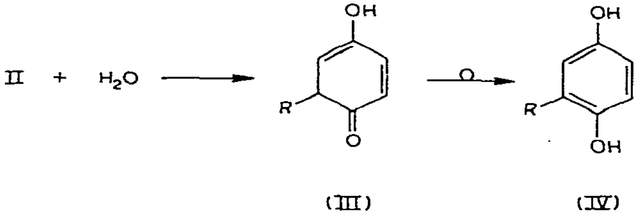
Iodine[5] and galvinoxyl[3] have been used successfully to inhibit extremely fast free radical reactions of organoboranes. Indeed, we find that the addition of iodine



(2)



(3)



(4)

effectively inhibits the otherwise fast addition of triethylborane to *p*-benzoquinone. Galvinoxyl also inhibits the reaction but to a lesser extent.

The results are shown graphically in Fig. 1.

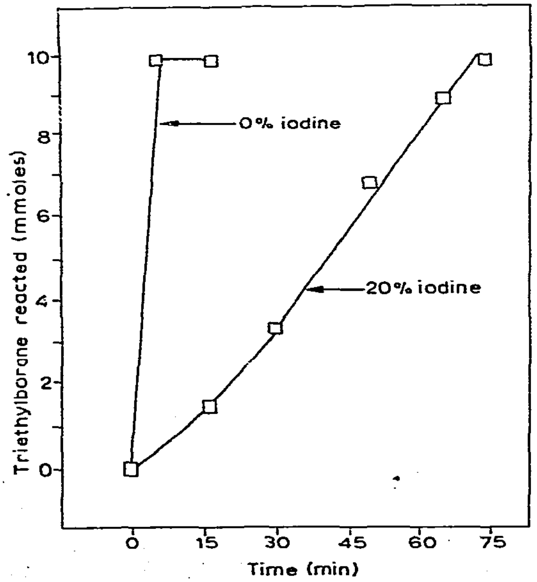


Fig. 1. Reaction of *p*-benzoquinone (0.33 *M*) with triethylborane (0.33 *M*) in diethyl ether at 25°. The effect of added iodine (in mol. %).

Consequently, the addition of trialkylboranes to *p*-benzoquinone must be a free radical 1,4-addition reaction. An important consequence of this fact is that the reaction should be applicable to other quinone substrates (such as 1,4-naphthoquinone, 1,2-naphthoquinone, 9,10-phenanthraquinone, etc.) which are reportedly unreactive toward trialkylboranes[2b]. It would appear that the behavior of the unreactive quinones might be the result of shorter chain length and inefficient initiation, analogous to the situation found for β-substituted α,β-unsaturated carbonyl compounds[6].

In support of this postulation, we wish to report that trialkylboranes react readily with 1,4-naphthoquinone in the presence of small quantities of oxygen (air) producing the corresponding 2-alkyl-1,4-naphthalenediols (after hydrolysis) in excellent yields.

The reaction appears to be one of wide generality, providing the alkylated naphthalenediols from a variety of structural types.

The following procedure is representative. A 200 ml three-necked flask fitted with an inlet carrying a rubber septum cap, a magnetic stirring bar, and a condenser was flushed with nitrogen. In the flask was placed a solution of 50 mmoles of borane in 25 ml of tetrahydrofuran. Then 150 mmoles (15.2 ml) of cyclohexene was added in 25 ml of tetrahydrofuran to form the tricyclohexylborane. The mixture was stirred at 50° for 3 h to complete the hydroboration. Then 60 mmoles (1.08 ml) of water was added, followed by a solution of 50 mmoles (7.8 g) of 1,4-naphthoquinone in 50 ml of tetrahydrofuran. Air[★] was then passed into the flask at the rate of 1 ml/min through a syringe needle placed through the rubber septum cap. GLC analysis indicated completion of the reaction within 20 minutes. The reaction mixture was then steam distilled to remove solvent, borinic acid, and boronic acid. The product was characterized by oxidation to the corresponding 2-cyclohexyl-1,4-naphthoquinone according to the method of Underwood and Walsh[7]. A 60% yield of 2-cyclohexyl-1,4-naphthoquinone (m.p. 86–88°) was isolated.

The experimental results are summarized in Table 1.

TABLE 1

CONVERSION OF OLEFINS INTO 2-ALKYL-1,4-NAPHTHALENEDIOLS BY REACTION OF THE CORRESPONDING ORGANOBORANES WITH 1,4-NAPHTHOQUINONE

Olefin	Product[a]	Yield[b,c] (%)	M.p. of corresponding quinone[d] (°C)
Ethylene	2-Ethyl-1,4-naphthalenediol	95	84–86
1-Butene	2-n-Butyl-1,4-naphthalenediol	85	44–45
Cyclohexene	2-Cyclohexyl-1,4-naphthalenediol	90	86–88

[a] All products were oxidized[7] and identified as the corresponding naphthoquinones. [b] By GLC analysis of the naphthoquinones. [c] The reactions were run as described in text except that a 10% excess of 1,4-naphthoquinone was employed. The yield is based on starting organoborane. [d] Melting points are uncorrected.

[★] The naphthoquinone in this reaction was twice recrystallized from dry, oxygen-free tetrahydrofuran. We have since discovered that air initiation is normally not required when commercial 1,4-naphthoquinone is utilized. In general, the reactions of organoboranes are instantaneous with commercial samples of naphthoquinone presumably due to sufficient oxygen for initiation being adsorbed on the surface of the quinone.

The facile reaction of organoboranes with 1,4-naphthoquinones makes available a practical new synthetic route to 2-alkyl-1,4-naphthalenediols and the corresponding alkylated naphthoquinones. Even more important is the possibility that other 'unreactive' quinone species may undergo similar reactions under suitable conditions. Such a study is in progress.

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