## NEW DIBENZOFURAN FORMATION FROM THE REACTIONS OF 1-CYCLOHEXENYLOXYDIBUTYL-BORANES WITH 2,3-DICHLORO-5,6-DICYANO-*P*-BENZOQUINONE (DDQ)

Kiyoshi Tanemura,\*a Koji Yamaguchi,<sup>b</sup> Hideo Arai,<sup>b</sup> Tsuneo Suzuki,<sup>a</sup> and Takaaki Horaguchi\*<sup>b</sup>

 School of Dentistry at Niigata, The Nippon Dental University, Hamaura-cho 1-8, Niigata 951, Japan
Department of Chemistry, Faculty of Science, Niigata University, Ikarashi, Niigata 950-21, Japan

Abstract-1-Cyclohexenyloxydibutylboranes, generated *in situ*, reacted with 2,3dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) to give dibenzofurans.

Oxidation of cyclohexanones to cyclohexenones *via* the reactions of silyl enol ethers with 2,3-dichloro-5,6dicyano-*p*-benzoquinone (DDQ) is one of the important synthetic transformations.<sup>1</sup> Recently, the intermediacy of carbon-oxygen adduct (2) and carbon-carbon adduct (3) was reported in the reaction of 1 with DDQ.<sup>2</sup> In connection with these reactions, it occurred to us to use vinyloxyboranes<sup>3</sup> instead of silyl enol ethers. In this paper, we wish to report new dibenzofuran formation by the reactions of 1cyclohexenyloxydibutylboranes with DDQ.



First, the reaction of 1-(4-t-butylcyclohexenyl)oxydibutylborane (5a) with DDQ was examined (Scheme

1). Vinyloxyborane (**5***a*), generated from the reaction of 4-*t*-butylcyclohexanone (**4***a*) (1.0 mmol) with dibutylboryl trifluoromethanesulfonate (triflate) (1.0 mmol) and diisopropylethylamine (1.0 mmol) in  $CH_2Cl_2$  (2.1 ml) *in situ*, was treated with DDQ (1.0 mmol) in  $CH_2Cl_2$  (13.3 ml) at room temperature for 1 h under nitrogen. 3,6-Di-*t*-butyldibenzofuran (**6***a*) was obtained in 29% yield together with large amounts of decomposed materials.<sup>4</sup> Other compounds such as carbon-oxygen adduct, carbon-carbon adduct, or 4-*t*-butylcyclohexenone were not detected.



Scheme 1

When 2.0, 3.0, and 4.0 equiv. of DDQ were employed, the yields of **6a** were 32, 34, and 23% yields, respectively. The reactions using various solvents were examined using 3.0 equiv. of DDQ. The results are summarized in Table 1. The use of less polar solvents such as  $CH_2Cl_2$  or  $C_6H_6$  showed better results. Similarly, vinyloxyboranes (**5b**) and (**5c**) reacted with DDQ to give the corresponding dibenzofurans (**6b**) and (**6c**) in low yields, respectively (Entries 5 and 6). On treatment of the other vinyloxyboranes derived from 2-methyl-, 3-methyl-, and 3,5-dimethyl-substituted cyclohexanones with DDQ, complete decomposition was observed.

| Entry | Ketone     | , Solvent                       | Time / h | Yield of 6 /%ª |
|-------|------------|---------------------------------|----------|----------------|
| 1     | <b>4</b> a | CH <sub>2</sub> Cl <sub>2</sub> | 2        | 34             |
| 2     |            | $C_6H_6$                        | 2        | 26             |
| 3     |            | Dioxane                         | 2        | 19             |
| 4     |            | MeCN                            | 2        | 10             |
| 5     | 4b         | $CH_2Cl_2$                      | 4        | 11             |
| 6     | <b>4</b> c | $C_6H_6$                        | 4        | 8              |
|       |            | 0 0                             |          |                |

**Table 1.** The reactions of vinyloxyboranes derived fromketones 4a-c with DDQ

alsolated Yields.

We suppose that dibenzofuran (6) is formed by the mechanism as shown in Scheme 2. The first step is a

single electron transfer (SET) process from vinyloxyborane (5) to DDQ. The resulting cation radical (7) would undergo dimerization to yield 8. Acid-catalyzed ring closure of 8 by DDQH<sub>2</sub> probably gives octahydrodibenzofuran (9).<sup>5</sup> Dehydrogenation of 9 by DDQ leads to dibenzofuran (6). From the reaction of vinyloxyborane (5a) with DDQ in CH<sub>2</sub>Cl<sub>2</sub> for 10 min, compound (9a) was isolated in 16% yield. Compound (9a) was also converted to 6a smoothly under the conditions employed.





## **REFERENCES AND NOTES**

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- 4. No reaction was observed when ketone (4a) was treated with DDQ in the absence of dibutylboryl triflate and diisopropylethylamine in  $CH_2Cl_2$  at room temperature for 1 h.
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