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

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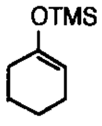
Abstract-1-Cyclohexenyloxydibutylboranes, generated *in situ*, reacted with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) to give dibenzofurans.

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



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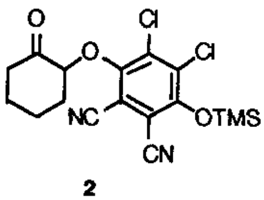

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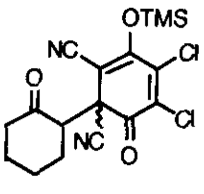

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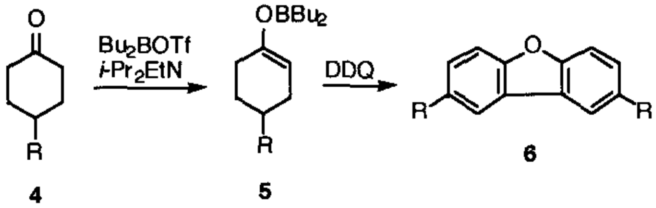
First, the reaction of 1-(4-*t*-butylcyclohexenyl)oxydibutylborane (**5a**) with DDQ was examined (Scheme

1). Vinyloxyborane (**5a**), generated from the reaction of 4-*t*-butylcyclohexanone (**4a**) (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 (**6a**) was obtained in 29% yield together with large amounts of decomposed materials.[4] Other compounds such as carbon-oxygen adduct, carbon-carbon adduct, or 4-*t*-butylcyclohexenone were not detected.



a, R = *t*-Bu, **b**; R = H, **c**; R = Me

Scheme 1

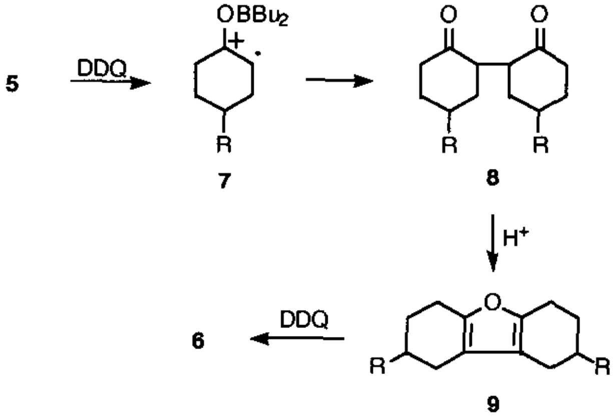
When 2.0, 3.0, and 4.0 equiv. of DDQ were employed, the yields of **6a** were 32, 34, and 23% yields, respectively. The reactions using various solvents were examined using 3.0 equiv. of DDQ. The results are summarized in Table 1. The use of less polar solvents such as CH_2Cl_2 or C_6H_6 showed better 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.

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

Entry	Ketone	Solvent	Time / h	Yield of **6** /%[a]
1	**4a**	CH_2Cl_2	2	34
2		C_6H_6	2	26
3		Dioxane	2	19
4		MeCN	2	10
5	**4b**	CH_2Cl_2	4	11
6	**4c**	C_6H_6	4	8

[a] Isolated 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 $DDQH_2$ probably gives octahydrodibenzofuran (**9**).[5] Dehydrogenation of **9** by DDQ leads to dibenzofuran (**6**). From the reaction of vinyloxyborane (**5a**) with DDQ in CH_2Cl_2 for 10 min, compound (**9a**) was isolated in 16% yield. Compound (**9a**) was also converted to **6a** smoothly under the conditions employed.



Scheme 2

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3. T. Inoue and T. Mukaiyama, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 174.
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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