Letters to the Editor

Chlorine dioxide as an oxidant for organoboron compounds

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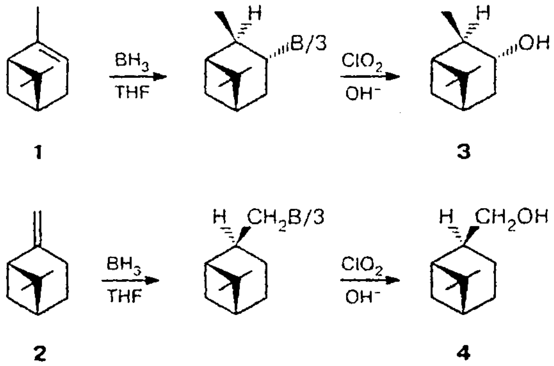
Chlorine dioxide (ClO_2) as a highly active oxidant is widely used in the cellulose-paper industry for cellulose bleach.[1] However, its use in organic synthesis is almost unknown. We have previously shown that ClO_2 oxidizes allyl alcohols,[2] dialkyl sulfides,[3] and organometallic compounds.[4] In this work, we described the use of this reagent for the oxidation of organoboron compounds.

Olefin and cycloalkene hydroboration followed by oxidation with hydrogen peroxide in alkaline media, amine *N*-oxides, or peracids is an important synthetic method of *cis*-hydration of double bonds that occurs contrary to the Markownikoff rule.[5] In addition to these methods, we demonstrated the possibility of using an aqueous solution of ClO_2 as an oxidant of organoboranes that formed by the hydroboration of α-pinene (**1**) (*ee* 37%) and β-pinene (**2**) (*ee* 70%) to isopinocampheol (**3**) and *cis*-myrtanol (**4**), respectively (Scheme 1).

Scheme 1



Hydroboration of **1** and **2** was carried out in THF using $LiBH_4$ and concentrated H_2SO_4 by the known procedure.[6] Then a 3 *N* aqueous solution of NaOH (0.33 mol-equiv.) was added to the reaction mixture, and the resulting solution was divided into two equal portions. One portion was oxidized with 30% H_2O_2. An aqueous solution of ClO_2 (0.1—0.2 mol-equiv., 3.5—4.5 g L^{-1}) was added dropwise to the second portion for 1.5—3 h. Then the reaction products were extracted with diethyl ether, washed with water, and dried with $MgSO_4$. The yield of the residues after the evaporation of the solvents was 87—89%. According to the GLC data, both reaction mixtures were virtually identical. To isolate pure samples of alcohols, column chromatography on neutral Al_2O_3 (Brockmann II activity) was used (hexane—diethyl ether (10 : 1) as the eluent).

The ^{13}C NMR and IR spectra of isolated isopinocampheol and *cis*-myrtanol coincide with the published data. The optical densities of compound **3** ($[\alpha]_D^{20}$ −13.5° (*c* 0.8, EtOH), *ee* 39%) and **4** ($[\alpha]_D^{20}$ −14.9° (*c* 0.8, EtOH), *ee* 71%) correspond to those of the starting

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α- and β-pinenes (**1** and **2**). Thus, the oxidation of organoboranes with chlorine dioxide proceeds in a high yield, as for the use of H_2O_2 in an alkaline medium, and virtually does not give by-products.

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