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# REACTION OF LITHIUM TRIALKYLVINYLBORATES AND OXIRANES
# A NOVEL SYNTHESIS OF 1,4-DIOLS

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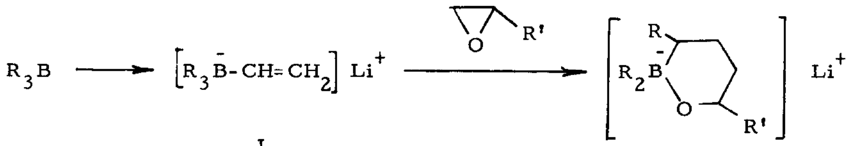
Trialkylalkynylborates have been shown to be useful as a tool in organic synthesis.[1-5] In continuation of studies on the chemistry of tetracoordinated boron compounds, this paper describes that the reaction of lithium trialkylvinylborates (I) with oxiranes followed by oxidative work-up produces 1,4-alkanediols (IV).

To a stirred solution of vinyllithium (5.0 mmol in 10 ml of ether) maintained under argon atmosphere at 0°, tributylborane (0.91 g, 5.0 mmol) was added. The resulting solution was stirred for 30 min. at 25°, added with 0.58 g (10 mmol) of methyloxirane at 0°, and the mixture was stirred at room temperature for 10 hr. Glc and ms analyses of the reaction mixture indicated the formation of an oxaborinane (III) ($M^+$, m/e 210). This was explained by assuming the thermolysis of a cyclic borate II upon glc injection.[6]

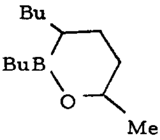
Usual oxidative work-up of the reaction mixture with alkaline hydrogen peroxide gave 2,5-nonanediol (IV. R=Bu, R'=Me) (bp 130°/4 mm)[7] in 93% yield.[8] Triisopropylborane afforded analogously 6-methyl-2,5-heptanediol (IV. R=i-Pr, R'=Me) (bp 110°/4 mm)[7] in quantitative yield. Oxirane itself reacted with I (R=Bu) to provide 1,4-octanediol (IV. R=Bu, R'=H) (bp 125°/4 mm)[7] in quantitative yield. Cyclohexene oxide reacted with I (R=Bu) at 50° for 12 hr to give 2-(2-hydroxyhexyl)-1-cyclohexanol (V) (bp 137°/0.3 mm) in 77% yield.[9]

As a trialkylborane is prepared from the respective olefin by hydroboration,[10] this method opens up a convenient way to the reductive 1,4-dihydroxyalkylation of an olefin.

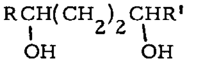


I

II

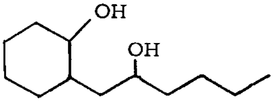


III



$$\underset{\textstyle OH}{RCH}(CH_2)_2\underset{\textstyle OH}{CHR'}$$

IV



V

The above described diol synthesis proved to be a key step in the preparation of cyclopentenones. Dihydrojasmone was prepared in this way: To a solution of trihexylborane prepared from 15.0 mmol of 1-hexene and 5.0 mmol of borane in 4 ml of THF, a solution of vinyllithium (5.0 mmol in 10 ml of ether) was added at 0° under argon atmosphere. The reaction mixture was treated with methyloxirane as described above and the subsequent oxidation gave 2,5-undecanediol (IV. R=hexyl, R'=Me) (bp 123-6°/3 mm) in 85% yield (purity 89%).[11] Jones oxidation followed by alkaline treatment afforded dihydrojasmone (bp 135°/7 mm)[7] (purity more than 95%) in 51% yield.

## REFERENCES AND REMARKS

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2. M. Naruse, K. Utimoto, and H. Nozaki, Ibid., 1847 (1973).
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4. Preparation and properties of alkali-metal trialkylalkynylborates: P. Binger, G. B G. Bendikt, G. W. Rotermund, and R. Koster, Liebigs Ann. Chem., **717**, 21 (1968), P. Binger and R. Köster, Synthesis, 309 (1973) and references cited therein.
5. A. Suzuki, N. Miyaura, S. Abiko, M. Itoh, H. C. Brown, J. A. Sinclair, and M. M. Midland, J. Am. Chem. Soc., **95**, 3080 (1973).
6. Similar thermolysis was reported in the case of oxaborinene formation (ref. 3).
7. Kugelrohr was used for distillation and the boiling point refers to the bath temperature
8. Trimethylsilyl ether of the diol was gas-chromatographically homogeneous (Silicon DC HVSG and PEG-20M). Whether this diol is one of the possible two diastereomers or a mixture is still uncertain.
9. The stereochemistry was assumed to be trans.
10. G. Zweifel and H. C. Brown, Org. Reactions, **13**, 1 (1963).
11. Gas chromatogram of the trimethylsilyl ether indicated that the product was a mixture of 2,5-undecanediol (89%) and 6-methyl-2,5-decanediol (11%). This ratio corresponds to that of 1-hexyl and 2-hexyl groups in prepared trihexylborane (ref. 10).