

PORT DOCUMENTATION PAGE

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| 19. ABSTRACT (Continue on reverse if necessary and identify by block number)<br><br>see attached report  |   |   |                         |
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OFFICE OF NAVAL RESEARCH

FINAL REPORT

for

Contract N00014-86-K-0547

Physical and Chemical Characteristics of Organoboranes



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**Personnel**

**Period on the Budget**

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|----------------|--------------------|
| R. K. Dhar     | 10/1/86 - 9/30/88  |
| S. Swaminathan | 8/5/86 - 6/30/88   |
| P. Pandiarajan | 12/1/86 - 5/31/87  |
| C. Zhao        | 10/1/87 - 10/18/88 |
| M. Srebnik     | 1/1/88 - 9/30/88   |
| G. Rajendran   | 2/1/88 - 7/31/88   |

**Technical Reports and Journal Articles**

**Technical Reports**

1. Enantioselective Ring-Cleavage of *meso*-Epoxides with B-Halodiisopinocampheylboranes  
N. N. Joshi, M. Srebnik and H. C. Brown
2. A Comparative Study of Dialkylboron Chlorides and Triflates for the Enolization of Ketones. The Controlled Stereospecific Synthesis of Either [*E*]- or [*Z*]-Enol Borinates  
H. C. Brown, B. Singaram, R. K. Dhar, P. K. Pandiarajan and R. K. Dhar
3. Enantioselective Ring-Cleavage of *meso*-Epoxides with B-Halodiisopinocampheylboranes  
N. N. Joshi, M. Srebnik and H. C. Brown  
Oral presentation at the 146th Meeting of the American Chemical Society in Los Angeles, CA, September 25-30, 1988

**Journal Articles**

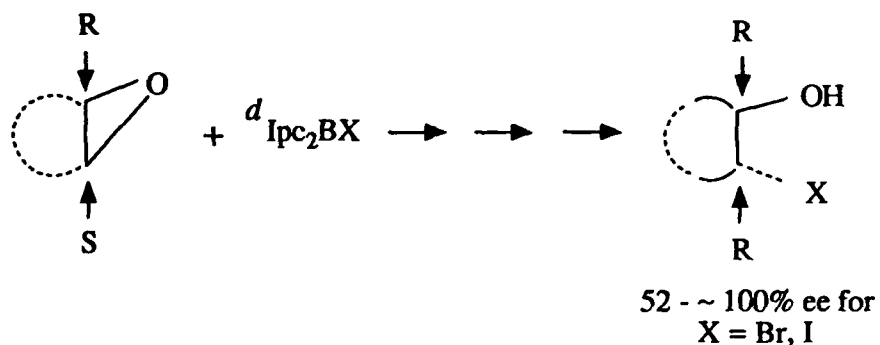
1. Enantioselective Ring-Cleavage of *meso*-Epoxides with B-Halodiisopinocampheylboranes  
N. N. Joshi, M. Srebnik and H. C. Brown  
*J. Am. Chem. Soc.* **1988**, *110*, 6246

**Summary of Accomplishments**

1. Enantioselective Ring Cleavage

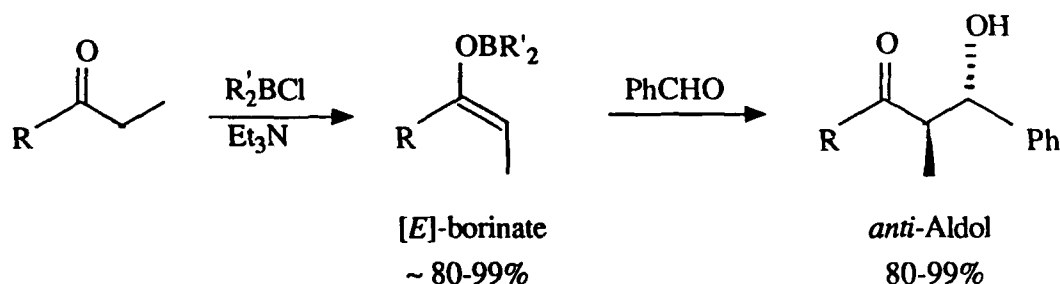
This subject has been detailed in Technical Reports (1), April 26, 1988, and (3), May 18, 1988. We have succeeded in obtaining optically active 1,2-halohydrins from *meso*-epoxides and chiral organoboranes. This is the first time such an asymmetric transformation has been accomplished.

*epoxides. (1988) ←*



## 2. Enol Borinates

This topic was the subject of Technical Report (2), May 13, 1988. In essence we have found conditions for obtaining [*E*]-enol borinates from ketones and readily available dialkylchloroboranes.



Reaction of the [*E*]-enol borinate with an aldehyde then gives the *anti*-aldol product. This methodology therefore complements the known process of obtaining [*Z*]-enol borinates from ketones and dialkyl boron triflates, which in turn provide *syn*-aldol products.

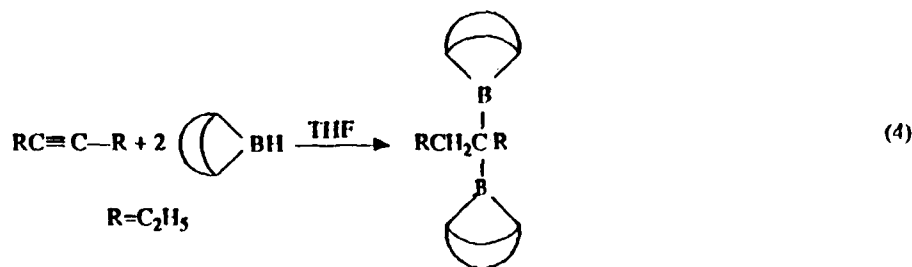
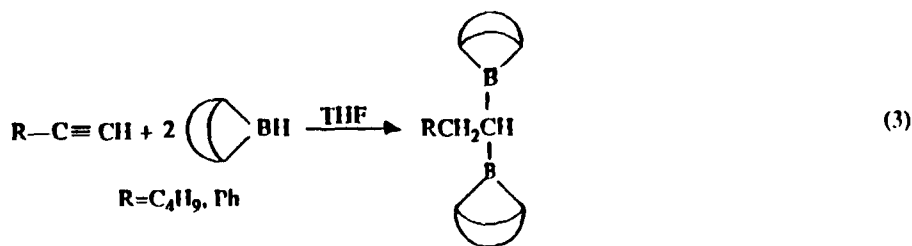
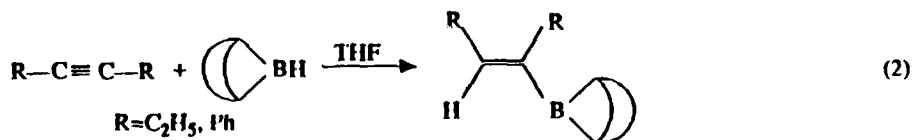
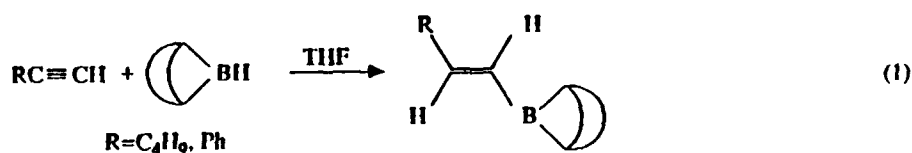
## 3. Hydroboration of Alkenes

This project was only briefly covered in the End-of-the-Year Reports (July 21, 1987 and July 22, 1988) and therefore will now be presented in greater detail.

Monohydroboration of symmetrically substituted internal alkynes, such as 3-hexyne and diphenylacetylene, with an equivalent of 9-BBN can be carried out at 0°C and 25°C respectively, producing the B-vinyl derivatives in 95-98% yields. The dihydroboration of 3-hexyne (0.25 *M*) with 2 equiv of 9-BBN (0.5 *M*) can only produce 56% of *gem*-dibora derivatives with 44% of B-vinyl derivatives at 25°C. However, the formation of *gem*-dibora derivatives can be improved by increasing the temperature (65°C) and concentration (0.75 *M*). The reaction of diphenylacetylene with 2 equiv of 9-BBN can only produce B-vinyl derivatives at 25°C, with no dihydroborated product. The dihydroboration of terminal alkynes, such as 1-hexyne and phenylacetylene, with 2 equiv of 9-BBN can produce *gem*-dibora derivatives in 81-90% yields. But the monohydroboration of 1-hexyne and phenylacetylene with an equivalent of 9-BBN can only

provide a mixture of B-vinyl and *gem*-dibora derivatives in 64:36 and 76:24 respectively. Fortunately, the monohydroboration of 1-hexyne with 9-BBN can be improved by use of 100% of excess of terminal alkyne, making possible the preparation of the corresponding B-[E]-1-hexenyl-9-BBN in 85% yield with no dihydroborated product. But in the case of phenylacetylene, the monohydroboration can only be improved to 83:17 from 76:24.

No general synthesis of B-vinyl and dibora derivatives has been studied in detail using various hydroborating agents and alkynes. Consequently, a systematic study was undertaken to prepare various B-alkenyl and dibora derivatives from representative alkynes using 9-BBN (eqs 1-4).



All yields were  $\geq 80\%$ . The products were confirmed by conversion to the corresponding aldehydes.