Tetrahedron Letters No. 12, pp 1019 - 1022, 1977. Pergamon Press. Printed in Great Britain.

# NOVEL BORATE ANION-ASSISTED CYCLIZATION. FACILE REARRANGEMENT OF 1-CYCLOPROPYLIDENEALKYLBORANES TO HOMOPROPARGYLBORANES

Ronald E. Merrill* and Judith L. Allen
Department of Chemistry, Rochester Institute of Technology
Rochester, New York 14623

Akiva Abramovitch and Ei-ichi Negishi*
Department of Chemistry, Syracuse University
Syracuse, New York 13210

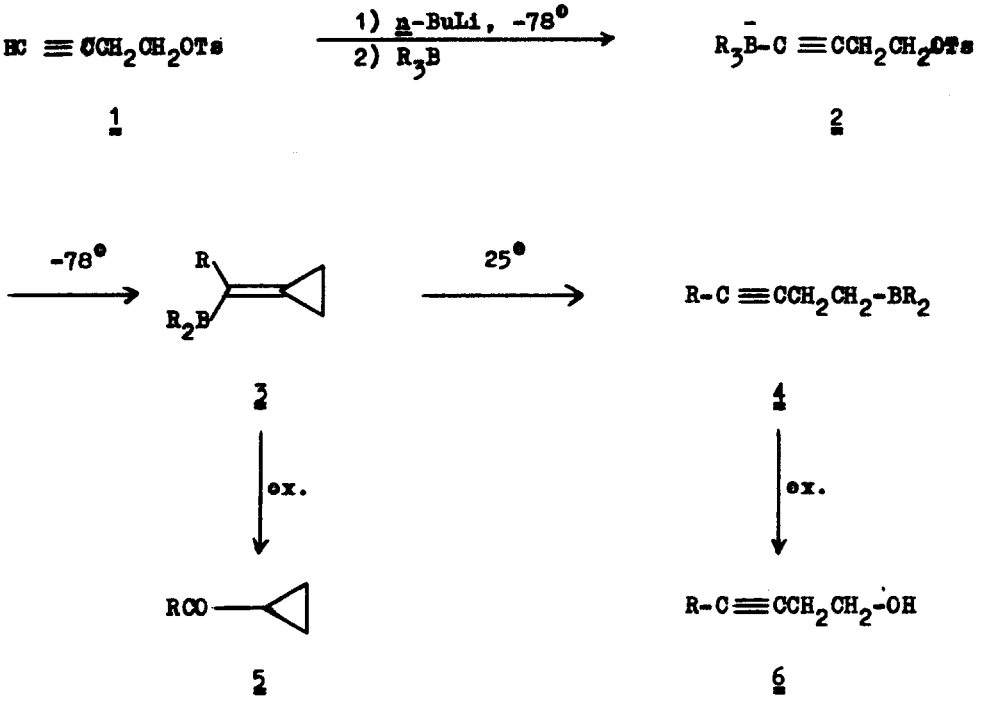
(Received in USA 8 November 1977; received in Uk for publication 9 February 1977)

Cyclization by means of intramolecular electrophilic attack on an alkene or alkyne is a powerful and general synthetic method.[1] Its major deficiency is the difficulty of efficiently trapping the cationic intermediate. We have found that this cyclization can be assisted by combining it with a borate anion rearrangement.[2-4]

Treatment of 4-tosyloxy-1-butyne[5] (1) at -78° with n-butyllithium, followed by addition of a trialkylborane at -78°, gives an organoborane intermediate which, on prompt oxidation by the addition of 3M NaOAc and 30% $H_2O_2$ below -20°, provides the corresponding cyclopropyl ketone (2) in 55-75% isolated yields. Although our attempts to characterize directly the organoboron intermediates have not been successful due to their instability, the mechanistic path shown in Scheme I, involving a 1,2-migration analogous to those proposed for related reactions of alkynylborates, accomodates nicely the observed results. As in other migration reactions of this type, the group R appears to migrate with complete retention of configuration, as indicated by the exclusive formation of the exo isomer of cyclopropyl 2-norbornyl ketone (clearly distinguishable from the endo isomer by $^{13}C$ NMR.)

If the reaction mixture is allowed to warm to room temperature, a different product, the alkynyl alcohol 6, emerges. By controlling the timing and temperature of oxidation, the ratio of 5 to 6 can be varied; the total product yield remains essentially constant. For the case where R = exo-2-norbornyl, reaction for about six hours at 25° gives exclusively the alkynyl alcohol. The products 5 and 6, once formed, do not interconvert under these conditions. We therefore conclude that the reaction must involve an unprecedented isomerization of the presumed borane intermediate 3 to the ring-opened borane 4.[6] Presumably the driving force for this unexpected rearrangement is provided by relief of the strain in 3. Although the homopropargyl alcohols 6 are of limited synthetic utility, it should be noted that boranes of type 4 are not readily available by hydroboration.

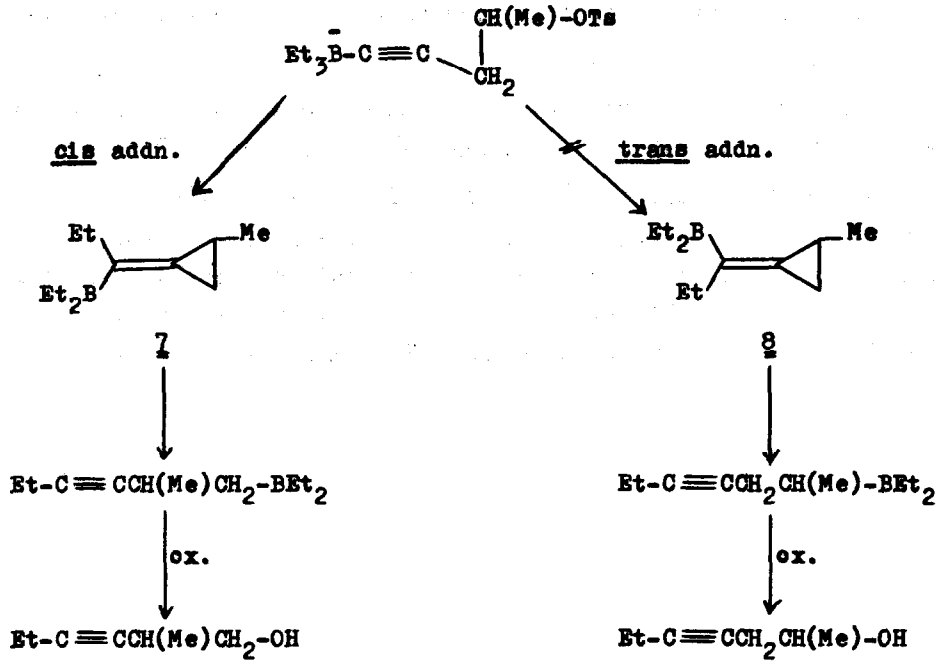
Scheme I




R = ethyl, n-butyl, n-hexyl, exo-2-norbornyl

The rearrangement of 3 to 4 may be viewed as analogous to the known rearrangement of allylic boranes.[7] However, it is not clear whether this rearrangement is concerted or stepwise. In this connection, the following observation is worth noting. When 1-lithio-4-tosyloxy-1-pentyne was reacted with triethylborane, immediate workup gave a 71% yield of trans-2-methylcyclopropyl ethyl ketone. When the oxidation was performed after 28 hours at room temperature, the only $C_7$ product was 2-methyl-3-hexyn-1-ol (70% yield). None of the isomeric 4-heptyne-2-ol could be detected by PMR. If the rearrangement occurs by a concerted, four-center mechanism, these results imply exclusive formation of the intermediate (7) arising from cis addition to the triple bond, rather than 8. This would accord with a very recently proposed set of cyclization rules,[8] according to which trans addition in this cyclization should be disfavored.

Scheme II




Acknowledgment. Support of this work by the Research Corporation, the National Science Foundation (MPS75-06106), Rochester Institute of Technology, and Syracuse University is gratefully acknowledged.

## REFERENCES AND FOOTNOTES

1. For a discussion of some of the characteristics of this reaction see: W. S. Johnson, Accounts Chem. Res. 1, 1 (1968).

2. (a) P. Binger and R. Köster, Tetrahedron Letters 1901 (1965); (b) A. Pelter, C. R. Harrison, and D. Kirkpatrick, J. C. S. Chem. Commun. 544 (1973); (c) A. Pelter, C. Subramanyam, R. J. Lamb, K. J. Gould, and C. R. Harrison, Tetrahedron Letters 1633 (1975).

3. For a review of the reactions of organoborates, see: E. Negishi, J. Organometallic Chem. 108, 281 (1976).

4. For cyclization reactions of trialkylboranes, see: H. C. Brown, "Boranes in Organic Chemistry," Cornell University Press, Ithaca, New York, 1972.

5. The mesylate may also be used.

6. For a similar rearrangement involving an oranomagnesium species, see: J.-L. Deroque and F.-B. Sundermann, J. Org. Chem. 39, 1411 (1974).

7. B. M. Mikhailov, Organometallic Chem. Rev. A 1, (1972).

8. J. E. Baldwin, J. Cutting, L. Silberman, J. Reiss, J. DeBernardis, W. Dupont, and R. Thomas, presented at the 7th Northeast Regional ACS meeting, August 8-11, 1976, Albany, New York. Part of this material has since been published: Jack E. Baldwin, J. C. S. Chem. Commun. 734 (1976).