CHEMISTRY LETTERS, pp. 485-488, 1974. Published by the Chemical Society of Japan

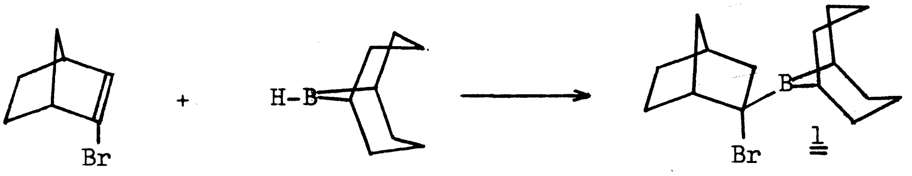
AN UNUSUAL DIRECTIVE EFFECT IN THE HYDROBORATION OF 2-BROMONORBORNENE WITH 9-BORABICYCLO[3.3.1]NONANE

Yoshinori YAMAMOTO, Hiroo TOI, and Ichiro MORITANI
Department of Chemistry, Faculty of Engineering Science
Osaka University, Toyonaka, Osaka 560

Hydroboration of 2-bromonorbornene with 9-borabicyclo[3.3.1]nonane (9-BBN) places the boron atom predominantly on the beta-position to the bromine substituent. On the other hand, in the hydroboration of 2-chloronorbornene the boron goes alpha to the chlorine substituent. The directive effect of the bromine is discussed.

It is reported that halo-substituents such as chlorine and bromine exert a directive influence favoring alpha-attack in the hydroboration of 1-halo-1-alkenes.[1)] The preference for alpha-attack is attributed to inductive effect of halogen atoms. For example, hydroboration of 2-chloronorbornene with diborane results in 82% alpha-attack and 18% beta-attack.[1b)]

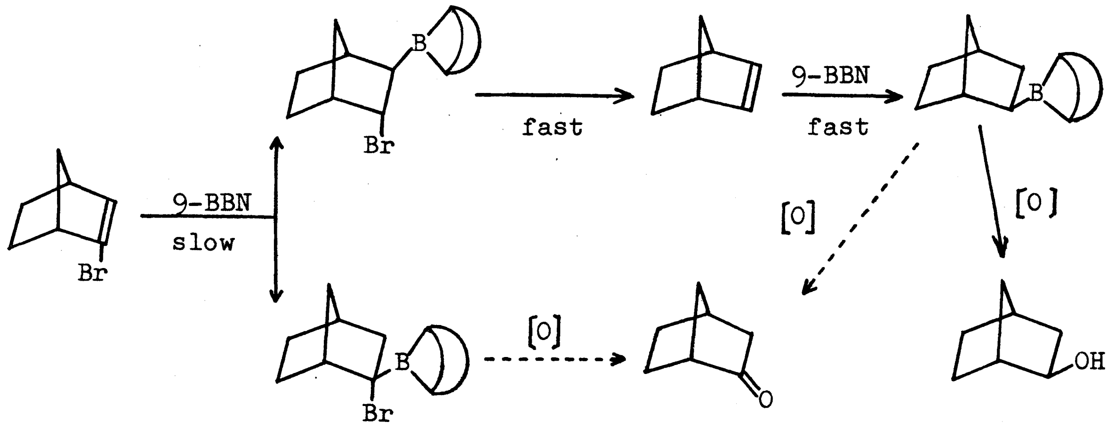
In the course of study on a series of alpha-bromoorganoboranes,[2)] it was required to prepare *endo*-alpha-bromonorbornyl-9-borabicyclo[3.3.1]nonane (**1**) in order to elucidate the stereochemistry of alkyl migration in alpha-bromotrialkylboranes. It appeared that the reaction of 2-bromonorbornene with 9-BBN would meet this purpose in view of both the directive influence of halogen atoms[1)] and *exo*-attack of 9-BBN to norbornene[3)] (eq 1).



(1)

Accordingly, 2-bromonorbornene (5 mmol) was treated with 9-BBN (5 mmol) in 20 ml of tetrahydrofuran at 20°C under nitrogen atmosphere. To our surprise, however, the reaction did not give the desirable product, but instead taking an another path. After stirring at this temperature for 24 hr, the reaction mixture was oxidized with an alkaline hydrogen peroxide. Glpc analysis revealed the formation of norbornanol (38 %), norcamphor (<2 %), and the recovery of 2-bromonorbornene (59 %).

The fact that so much olefin is recovered indicates a relatively slow reaction of 9-BBN to the 2-bromonorbornene. Norbornanol must be produced via elimination-rehydroboration of beta-bromonorbornyl-9-BBN as is shown in eq 2.1) This stage is probably faster than the initial hydroboration step of 2-bromonorbornene. In fact, the starting olefin is recovered in 59% yield, indicating some 79-82 % of 9-BBN is consumed and some 18-21 % of the agent rests unreacting. Actually, the addition of water to the reaction mixture causes evolution of an essentially quantitative amount of hydrogen.



(2)

Further support for the elimination-rehydroboration step is obtained by the hydroboration of 2-bromonorbornene with dicyclohexylborane instead of 9-BBN. Hydroboration with dicyclohexylborane offers high regioselectivity, but the agent reacts only sluggishly with internal and cyclic olefins.4) Therefore, it seems that the rehydroboration stage will be slower with dicyclohexylborane than with 9-BBN. Indeed, the intermediate norbornene is isolated in the reaction of 2-bromonorbornene with dicyclohexylborane.

The origin of the minor product, norcamphor, is not obvious at the present time. This may be a byproduct in the oxidation of norbornyl-9-BBN. In fact, it is observed that the oxidation of trinorbornylborane is accompanied with formation of a trace amount of norcamphor.5) Alternatively, this may be the oxidation product of alpha-bromonorbornyl-9-BBN, provided that the migration of the cyclooctyl-boron bond were more sluggish than the oxidation of the norbornyl-boron bond under the reaction condition.2)

Consequently, these results indicate that at least 93 % of the boron atom goes beta, at most 7 % alpha to the bromine substituent. Hitherto known result supports that the halogen substituents such as chlorine and bromine exert an attractive influence for the boron,[1)] though there is an only exceptional report.[6)] The present unusual directive effect might be a reflection of the utilization of 9-BBN instead of diborane. Accordingly, we undertook to make this point clear.

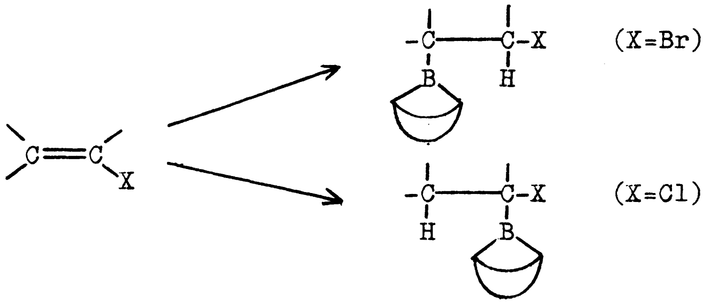
Hydroboration of 2-chloronorbornene (5 mmol) with 9-BBN (5 mmol) in 20 ml of tetrahydrofuran, followed by oxidation, was performed under the identical condition. Glpc analysis revealed the recovery of 18 % of 2-chloronorbornene, indicating that the reaction was relatively faster than that of the bromo-derivative. Norbornanol ($<$1 %) and norcamphor (2 %) were detected, and the formation of other low boiling materials was not observed.[7)] If the boron would add to the beta-position to the chlorine, norbornanol, norbornene, norbornylchlorohydrin, or norbornylepoxide would be produced after the oxidation.[1b)] However, such products were not detected except a trace amount of norbornanol.

Consequently, this result indicates the boron of 9-BBN predominantly goes to the alpha-position of the chlorine substituent, which is not contradictory to the Pasto's result with diborane.[1b)] Therefore, there appears no possibility that the unusual directive effect may be attributed to the difference of the hydroborating agent. The unusual observation should be ascribed mainly to the bromine substituent.

Previous investigations in the hydroboration of vinyl halides include several kinds of vinyl chloride[1)], and an only vinyl bromide, beta-bromostyrene.[1a)] It seems that the conclusion for directive effect of halogen atoms has generality for chlorine. However, it appears dangerous to assume that bromine may show the same tendency for the directive effect as chlorine from the result of beta-bromostyrene. The phenyl substituent may exert a delicate influence in the hydroboration. Moreover, in those hydroboration studies with diborane, the major inconvenience is the facile occurrence of alpha-transfer and elimination-rehydroboration, making the interpretation of the results difficult.[1)] This difficulty is avoided by the utilization of 9-BBN.

We wish to tentatively propose a following interpretation for the present observation. Hydroboration is a delicate balance of electronic and steric factors. Inductive effect of bromine is less powerful than that of chlorine.[8)] Furthermore, bromine is sterically more bulky than chlorine. Consequently, the blend of these factors may cause the unusual result.

Although other explanations may be presented in view of the mechanism of hydroboration, it is evidently suggested that we are in position to convert vinyl halides into alpha- and beta-haloboranes by merely controlling the halogen substituent (eq 3). The easy availability of the positional isomers from the same kind of vinyl halides is promising for further synthesis via these intermediates. We are continuing to investigate these possibilities.



(3)

References

1)(a) D. J. Pasto and S. R. Snyder, J. Org. Chem., 31, 2773(1966); (b)D.J. Pasto and J. Hickman, J. Amer. Chem. Soc., 89, 5608(1967); (c) H. C. Brown and R. L. Sharp, ibid., 90, 2915(1968).

2)(a) H. C. Brown and Y. Yamamoto, ibid., 93, 2796(1971); (b) H. C. Brown and Y. Yamamoto, Chem. Commun., 1535(1971); (c) H. C. Brown and Y. Yamamoto, ibid., 71(1972); (d) H. C. Brown, Y. Yamamoto, and C. F. Lane, Synthesis, 304(1972); (e) H. C. Brown and Y. Yamamoto, ibid.,699(1972);(f)Y. Yamamoto and H.C. Brown, Chem. Commun.,801(1973);(g)Y.Yamamoto and H.C.Brown,J. Org.Chem.,in print.

3) E.F. Knights and H. C. Brown, J. Amer. Chem. Soc., 90, 5281(1972).

4) H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962.

5) unpublished observation; see also D. J. Pasto, S. K. Arora, and J. Chow, Tetrahedron, 25, 1571(1969).

6) S. J. Cristol, F. P. Parungo, and D. E. Plorde, J. Amer. Chem. Soc., 87, 2870 (1965).

7) The main product presumably results from the migration of the alpha-chloroderivative. This is under investigation in connection with stereochemical study of the protonolysis of the intermediate.

8) J. March, "Advanced Organic Chemistry," McGraw Hill, New York, N. Y., 1968.

(Received March 18, 1974)