

served splittings are those expected for the products of *trans* addition, IIa and IIb. To confirm this assignment, the bromide and acetate were separated by v.p.c. and the bromide was converted to the corresponding Grignard reagent which rapidly loses its stereochemical configuration. The bromide was then regenerated by allowing the Grignard reagent to react with bromine. The recovered bromide showed, in addition to the original 3.5 c.p.s. doublet, a new doublet with a spacing of 8.7 c.p.s. centered approximately 0.5 c.p.s. upfield from the original doublet. The new signal clearly derives from bromide IIIa.

Additions were carried out at several temperatures and the product compositions were estimated by v.p.c. and n.m.r. analysis. The results are summarized in Table I. It seems probable that the acetate formed is also the product of *trans* addition, but this must remain tentative until the splitting for the isomeric acetate, IIIb, corresponding to *cis* addition, has been determined. The current results are in accord with earlier studies by Winstein and Holness⁷ of the addition of formic acid to 4-*t*-butylcyclohexene, where the results indicated a *trans* addition process. Moreover, it has been independently found that deuterium bromide adds *trans* to cyclohexene-3,3,6,6-*d*₄.⁸

TABLE I

<i>T</i> °C.	% bromide	% acetate	% bromide formed by <i>cis</i> addition
15	91	9	<4
25	88	12	<4
40	85	15	<5
60	76	24	<6

The finding of *trans* addition of hydrogen bromide to cyclohexene serves to offset the many recent examples of *cis* addition to olefins and further emphasizes that the stereochemistry of electrophilic additions is a sensitive function of olefin structure. A discussion of the mechanistic significance of these results is deferred until detailed kinetic studies, now in progress, have been completed.

Acknowledgment.—We gratefully acknowledge support of this research under Grant GP-2647 from the National Science Foundation.

(7) S. Winstein and N. J. Holness, *J. Am. Chem. Soc.*, **77**, 5562 (1955).

(8) Private communication from Professor Saul Wolfe, Queens University, Kingston, Ontario.

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Isolation of the Hexahydroclovohexaborate(2−) Anion, B₆H₆^{2−}

Sir:

The reaction of sodium borohydride with diborane has been reported to yield B₃H₃[−], B₁₀H₁₀^{2−}, B₁₁H₁₄[−], and B₁₂H₁₂^{2−}, and some of these can be isolated in high yields by controlling the conditions of the reaction.^{1,2}

(1) I. A. Ellis, D. F. Gaines, and R. Schaeffer, *J. Am. Chem. Soc.*, **85**, 3885 (1963).

(2) H. C. Miller, N. E. Miller, and E. L. Muetterties, *ibid.*, **85**, 3885 (1963).

We now report the preparation and isolation of a new boron hydride anion, B₆H₆^{2−}.

Diborane was added to a diethylene glycol dimethyl ether (diglyme) solution of sodium borohydride at 100° and the resulting solution refluxed for 16 hr. at 162°. The precipitate which formed during the reflux period was removed by filtration, dried, and dissolved in water. Tetramethylammonium chloride was added until precipitation occurred. Recrystallization gave tetramethylammonium hexahydroclovohexaborate(2−) in a yield which was equivalent to 5–10% of the total boron in the reaction system. *Anal.* Calcd. for C₈H₃₀B₆N₂: C, 43.81; H, 13.79; B, 29.61; N, 12.78. Found: C, 43.22; H, 13.72; B, 30.28; N, 12.75. The average molecular weight in water was found by vapor pressure osmometry to be 72 ± 2 (calcd., 219/3 = 73). The melting point exceeded 300°.

The ¹¹B n.m.r. spectral studies gave a symmetrical doublet with a chemical shift of 13 p.p.m. (relative to BF₃·Et₂O) and a coupling constant of 122 c.p.s. This is consistent with an octahedral configuration of boron atoms with each boron bonded to a single hydrogen atom.^{3,4} The octahedral structure has been fully confirmed in other laboratories by a complete three-dimensional X-ray study, the details of which will be published elsewhere.⁵

The infrared spectra of tetramethylammonium hexahydroclovohexaborate(2−) in Nujol and perchlorobutadiene show strong absorption at 4.13, 6.73, and 10.46 μ, moderate absorption at 3.33, 7.72, and 9.68 μ, and weak absorption at 5.62 and 5.90 μ. Three principal absorption bands for the cesium salt (4.13, 9.6, and 13.8 μ) are consistent with the octahedral symmetry of the anion.

The ammonium and potassium salts have also been prepared and analyzed. Silver and lead salts prepared by the addition of the hexahydroclovohexaborate(2−) anion to solutions of silver or lead nitrate were subject to detonation. The silver salt was extremely sensitive in the dry state.

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(3) W. H. Eberhardt, B. L. Crawford, Jr., and W. N. Lipscomb, *J. Chem. Phys.*, **22**, 989 (1954).

(4) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York, N. Y., 1963.

(5) Q. Johnson, R. Schaeffer, and G. Smith, future publication.

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Cesium Tropenylum Nonahydrodecaborate^{1,2}

Sir:

We wish to report the synthesis of cesium tropenylum nonahydrodecaborate as the first member of a new class of organoboron compounds.

(1) Supported by the Petroleum Research Fund and the National Science Foundation.

(2) (a) We will use the name tropenylum for the cationic substituent (C₇H₆⁺) which results from hydride abstraction from a tropenyl (C₇H₇−) substituent group. (b) The representation herein of the polyhedral decahydrodecaborate anion—a circle for the boron cage, with only the apical hydrogens shown—is used as an expedient until a formal notation for such species is adopted.