

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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RECEIVED SEPTEMBER 11, 1964

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.

Acknowledgments.—We wish to thank Dr. G. W. Campbell and Professor R. Schaeffer for valuable consultation, and R. M. Jeffs for laboratory assistance.

(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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RECEIVED SEPTEMBER 30, 1964

Cesium Tropenylum Nonahydrodecaborate^{1,2}

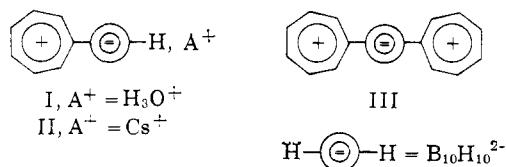
Sir:

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.

Reaction of hydronium decahydrodecaborate³ with excess tropenium bromide in aqueous solution gives a heavy maroon precipitate and a red-orange solution; this solution contains a 7.2% yield of hydronium tropenylum nonahydrodecaborate (I).^{2b} Concentration of this solution followed by treatment with cesium chloride yields 69% cesium tropenylum nonahydrodecaborate (II) as orange plates, no melting point or



decomposition below 360°; ultraviolet and visible spectrum (water): λ_{\max} 217 (ϵ 39,400), 262 (10,900), and 439 (13,600) m μ .

Anal. Calcd. for C₇H₁₅B₁₀Cs: C, 24.70; H, 4.44; B, 31.79. Found⁴: C, 24.39; H, 4.54; B, 31.95.

We have assigned the structure shown for this compound on the basis of the following observations: (1) the electronic spectrum is not that of a tropenium salt⁵ but strongly resembles that of a substituted tropenium ion,⁶ (2) the compound fails to give tropenium ion when extracted with 96% sulfuric acid but instead dissolves slowly to give a spectrum similar to that in water, (3) the long wave-length absorption—which we ascribe to electron transfer from the boron cage to the carbon ring in an internal charge transfer⁸—shows a strong hypsochromic shift with increasing solvent polarity (see Table I) which indicates a transition from a

TABLE I

Solvent	Absorption bands of II, m μ		
CH ₃ CN	222	265	513
50% CH ₃ CN-H ₂ O	221	263	485
H ₂ O	217	262	439
12 N HCl	217	262	427
96% H ₂ SO ₄	217	262	373

more polar to a less polar state on absorption of light which is hindered by solvation of a polar ground state, and (4) the infrared spectrum is in accord with the proposed structure; the B-H stretching band (2430 cm.⁻¹) has two shoulders (2520 and 2350 cm.⁻¹) and is not split as it is in the decahydrodecaborate anion, the boron cage bands (1010 and 975 cm.⁻¹) are diminished relative to the B-H compared to the free anion, and the

(3) Prepared from triethylammonium decahydrodecaborate generously furnished by M. Frederick Hawthorne.

(4) Analysis by Schwarzkopf Microanalytical Laboratory.

(5) W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **76**, 3202 (1954), report the spectrum of tropenium ion in water as λ_{\max} 275 (4350) and 280 (sh) m μ ; we find that the decahydrodecaborate anion only shows end absorption.

(6) H. J. Dauben, Jr., F. A. Gadecki, K. M. Harmon, and D. L. Pearson (*ibid.*, **79**, 4557 (1957)) and H. J. Dauben, Jr., and K. M. Harmon (unpublished work in Ph.D. Thesis of K. M. H., University of Washington, 1958) report, for example, the spectrum in 96% sulfuric acid⁷ of thiomethoxytropenium ion as λ_{\max} 220 (ϵ 19,500), 259 (14,400), and 383 (16,500) m μ and of iodotropenium ion as λ_{\max} 216 (ϵ 23,200), 263 (9300), 335 (sh), and 378.5 (5060) m μ .

(7) In cases where the ion is stable in water, the spectra of tropenium ions in water and sulfuric acid are similar.

(8) Similarly, examination of the shape and splitting of the long wave-length band of iodotropenium ion indicates that it arises from n- π^* electron transfer from substituent to ring.

C-H stretching (2920 (vw) and 2850 (sh) cm.⁻¹) and C-C single and double bond bands (1602 (w), 1493-1474 (s), 1429 (mw), 1358 (mw), 1277 (w), 1230 (m), and 1182 (m) cm.⁻¹) strongly resemble the pattern of tropone,⁹ an electronically similar compound. Examination of the infrared spectra of tropenium ion, halotropenium ions, tropone, and II indicates that double bonding from ring to substituent is important in both II and tropone, but is less so in II.

The acid I is an orange oil which has electronic and infrared spectra similar to that of II except for the inclusion of O-H bands in the infrared. We believe that it is formed by electrophilic attack of tropenium ion on decahydrodecaborate anion followed by hydride transfer from the cycloheptatrienyl nonahydrodecaborate ion so formed to tropenium ion; at least 1 mole of cycloheptatriene per mole of original decahydrodecaborate anion can be isolated from the reaction solution. Reaction of II with additional tropenium bromide in aqueous solution gives cycloheptatriene and maroon crystals believed to be bistropenylum octahydrodecaborate (III). This material is remarkably thermally stable and is insoluble in most solvents (slightly soluble in dimethyl sulfoxide). The infrared spectrum of III is very similar to that of II; however, the cage absorption is missing, the B-H band is a symmetrical spike, and the ratio of C-C double bond intensity to B-H intensity is 1.75 compared to 0.77 in II. Further characterization of this compound is in progress.

The precipitated material which represents the major product in the reaction of tropenium ion with hydronium decahydrodecaborate appears to contain both carbonaceous material and polymeric acids of -C₇H₅-B₁₀H₈- chain anions. When these are largely removed by continuous extraction with acetonitrile, a uniform maroon powder results with an infrared spectrum identical with that of III. Further purification and characterization is in progress.

(9) Y. Ikegami, *Bull. Chem. Soc. Japan*, **35**, 967 (1962), gives the most detailed analysis of the infrared spectrum of tropone.

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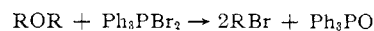
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RECEIVED SEPTEMBER 16, 1964

The Cleavage of Ethers by Triphenyldibromophosphorane

Sir:

We report herein a new method of ether cleavage which has obvious advantages over the strongly acidic conditions commonly, or the strongly basic conditions¹ sometimes employed. The reagent of our method is triphenyldibromophosphorane, and the over-all reaction of this with aliphatic ethers may be summarized by the equation



Illustrative results are given in Table I.

(1) For example, dialkyl ethers are split by secondary and tertiary alkyl lithium reagents (*cf.* H. Gilman, F. W. Moore, and O. Baine, *J. Am. Chem. Soc.*, **63**, 2480 (1941)), and diallyl ether is cleaved by metallic sodium (*cf.* R. L. Letsinger and J. G. Traynham, *ibid.*, **70**, (1948)).