

tion II yields a lifetime for  $H_3O$  in the fission recoil track of  $1.13/k_9$  or about  $10^{-9}$  sec.

The dependence of  $G_{H_2}$  on the concentration of  $NO_3^-$  for the decomposition of water by  $^{60}Co$   $\gamma$ -radiation, previously approximated<sup>12,13</sup> as a cube-root dependency, is quantitatively expressed by eq. III, but only for

$$1/G_{H_2} = 2.93 + 7.53[NO_3^-] \quad (III)$$

concentrations from 0.01 to 1.0  $M$ . Equation III yields a lifetime for  $H_3O$  in the spur of  $2.57/k_8$ , in excellent agreement with eq. I. The failure of eq. III to apply at concentrations less than 0.01  $M$  leads us to propose that  $H_2$  formation by  $^{60}Co$   $\gamma$ -radiation results from two processes: intraspur and interspur processes with  $G_{H_2} = 0.34$  for the former. In interspur processes, intermediates from one spur interact with intermediates from an adjacent spur before they escape into the bulk of the solution. The dependence of  $G_{H_2}$  on  $NO_3^-$  at concentrations less than 0.01  $M$  is consistent with both  $G_{H_2} = 0.11$  and a lifetime for  $H_3O$  of approximately  $300/k_8$  for interspur processes.

The new model for  $H_2$  formation leads us to propose an alternative viewpoint concerning the influence of pH on  $G_{e_{aq}^-}$ .  $H_{aq}^+$  reacts with those electrons,  $k_{10}[H_{aq}^+][e_{aq}^-]$ , which would otherwise disappear in spur processes. The lifetime for the  $e_{aq}^-$  in the spur is  $130/k_{10}$  or  $6 \times 10^{-9}$  sec. (originally reported<sup>14</sup> as  $0.01/k_{10}$  and attributed to  $H_2O^*$ ).

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### The Polar Addition of Hydrogen Bromide to Cyclohexene<sup>1</sup>

Sir:

In recent years a variety of examples of polar *cis* additions of acids and alcohols to olefins has been reported.<sup>2-5</sup> These include the addition of deuterium bromide to cyclohexene, which has been reported<sup>2</sup> to give 26, 31.5, 63, and 74% of *cis* adduct at 10, 25, 45, and 60°, respectively. This variation in stereochemistry with temperature seemed unusual to us and prompted us to re-examine this reaction. Our results are in substantial disagreement with the earlier findings. When cyclohexene-2,6,6- $d_3$  is allowed to react with hydrogen bromide in acetic acid, addition of acetic acid as well as hydrogen bromide occurs, and the addition is very predominantly *trans* at temperatures from 15 to 60°.

The stereochemistry of addition to cyclohexene-2,6,6- $d_3$  can be established from the n.m.r. spectra of

(1) This research was presented at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept., 1964.

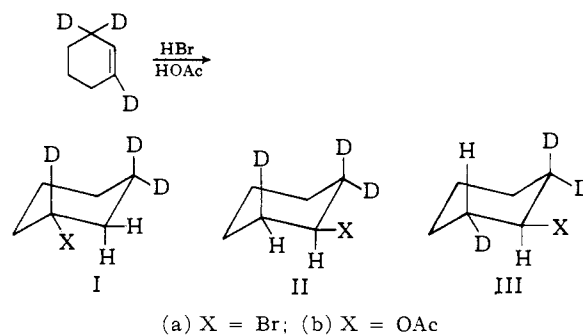
(2) J. V. Smirnov-Zamkov and G. A. Piskovitina, *Ukr. Khim. Zh.*, **28**, 531 (1962).

(3) M. J. S. Dewar and R. C. Fahey, *J. Am. Chem. Soc.*, **85**, 2245, 2248, 3645 (1963).

(4) S. J. Cristol, L. K. Gaston, and D. W. Johnson, *Tetrahedron Letters*, 185 (1963).

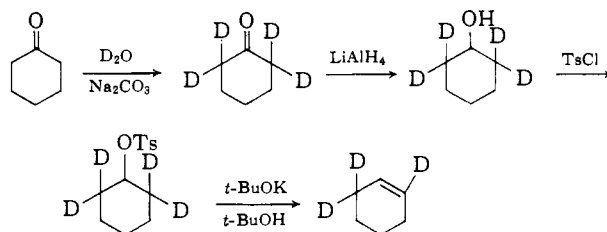
(5) H. Kwart and J. L. Nyce, *J. Am. Chem. Soc.*, **86**, 2601 (1964).

the products. The bromides Ia-IIIa and the acetates Ib-IIIb are possible products depending on the direction and stereochemistry of the addition. No low-



field resonance is expected for Ia or Ib, whereas IIa and IIb (from *trans* addition) and IIIa and IIIb (from *cis* addition) should give low-field doublets for the  $C_1$ -H resonance with expected splittings of 2-4 and 8-10 c.p.s., respectively. Complications due to coupling involving deuterium can be averted through the use of deuterium double irradiation.<sup>6</sup>

Cyclohexene-2,6,6- $d_3$  was prepared according to the following reaction sequence



In a typical addition experiment, 20 ml. of 0.5  $M$  hydrogen bromide in dry acetic acid, 0.5 ml. of cyclohexene-2,6,6- $d_3$ , and 10 mg. of 2,6-di-*t*-butyl-*p*-cresol (used to inhibit free-radical addition) were sealed in an ampoule and placed in a thermostated bath for 1-4 hr. The reaction was worked up in water by extracting with pentane. The pentane fraction was washed with dilute bicarbonate, dried over anhydrous sodium carbonate, and filtered. Evaporation of the pentane gave 75-95% crude yields of product. The polar character of the reaction was demonstrated by showing that addition of hydrogen bromide to 1-hexene in the presence of cyclohexene gave 2-bromohexane and cyclohexyl bromide, with no 1-bromohexane (the free-radical addition product) being formed.

Analysis of the reaction products, both by n.m.r. and by v.p.c., demonstrated the presence of both acetate and bromide. In control experiments it was shown that, under the reaction conditions, cyclohexyl bromide is not converted to cyclohexyl acetate, whereas cyclohexyl acetate is very slowly converted to the bromide. The n.m.r. spectrum of the addition product mixture showed broad signals at 4.67 (acetate) and 4.13 p.p.m. (bromide) downfield from TMS, which sharpened into doublets with 3.3 and 3.5 c.p.s. spacings, respectively, when the samples were simultaneously irradiated at the deuterium resonance frequency. The ob-

(6) A Nuclear Magnetic Resonance Specialties, Inc., Model SD-60 spin decoupler was used in conjunction with a Varian HR-60 spectrometer in these studies.

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 Holness<sup>7</sup> 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*<sub>4</sub>.<sup>8</sup>

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, B<sub>6</sub>H<sub>6</sub><sup>2−</sup>

Sir:

The reaction of sodium borohydride with diborane has been reported to yield B<sub>3</sub>H<sub>8</sub><sup>−</sup>, B<sub>10</sub>H<sub>10</sub><sup>2−</sup>, B<sub>11</sub>H<sub>14</sub><sup>−</sup>, and B<sub>12</sub>H<sub>12</sub><sup>2−</sup>, and some of these can be isolated in high yields by controlling the conditions of the reaction.<sup>1,2</sup>

(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, B<sub>6</sub>H<sub>6</sub><sup>2−</sup>.

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 C<sub>8</sub>H<sub>30</sub>B<sub>6</sub>N<sub>2</sub>: 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 <sup>11</sup>B n.m.r. spectral studies gave a symmetrical doublet with a chemical shift of 13 p.p.m. (relative to BF<sub>3</sub>·Et<sub>2</sub>O) 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.<sup>3,4</sup> 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.<sup>5</sup>

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<sup>1,2</sup>

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 (C<sub>7</sub>H<sub>6</sub><sup>+</sup>) which results from hydride abstraction from a tropenyl (C<sub>7</sub>H<sub>7</sub><sup>−</sup>) 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.