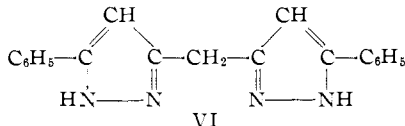


I showed, in addition to peaks corresponding to the methylene and vinyl hydrogens, three peaks with chemical shifts of 2.02, 2.05, and 2.30 p.p.m. which were assigned to the terminal methyl protons.<sup>5</sup>

The structure of the tetraketone was further supported by its reaction with excess hydrazine to form the dipyrazole VI, m.p. 218–219°, in 88% yield. *Anal.* Calcd. for C<sub>19</sub>H<sub>16</sub>N<sub>4</sub>: C, 75.97; H, 5.37; N, 18.66; mol. wt., 340. Found: C, 76.12; H, 5.24; N, 18.70; mol. wt., 312.



That the dipyrazole was VI, not the possible one from IV, was supported by its n.m.r. spectrum (in dimethyl sulfoxide using tetramethylsilane as an external standard) which showed peaks corresponding to the protons in the structural units NH (12.95 p.p.m.), C=CH (6.53 p.p.m.), and C-CH<sub>2</sub> (4.02 p.p.m.), but no peak indicative of the terminal methyl group as would be present in the dipyrazole of IV.

Studies are now in progress on other acylations of 1,3,5-triketones and on the related acylations and carbethoxylations. The mechanism of the reaction and the properties of the products will be investigated. Such products should be of interest in connection with the biosynthesis of many plant and mould products by the acetate-malonate (polyketide) route.<sup>6</sup>

**Acknowledgment.**—The authors wish to thank Dr. Walter L. Meyer of Indiana University for obtaining and interpreting the n.m.r. spectra of the ketones prepared in this study.

same solution gave, besides the aromatic proton peaks, only two major peaks which were assigned as above.

(5) Apparently, in chloroform solution an equilibrium exists between three enolic forms.

(6) See A. J. Birch, P. Fitton, D. C. C. Smith, D. E. Steere, and A. R. Stelfox, *J. Chem. Soc.*, 2209 (1963); A. J. Birch and F. W. Donovan, *Australian J. Chem.*, 6, 360 (1953); A. J. Birch, *Proc. Chem. Soc.*, 3 (1962).

DUKE UNIVERSITY  
DURHAM, NORTH CAROLINA

MARION L. MILES  
THOMAS M. HARRIS  
CHARLES R. HAUSER

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### A Convenient Preparation of B<sub>12</sub>H<sub>12</sub><sup>2-</sup> Salts<sup>1</sup>

Sir:

Studies of the B<sub>12</sub>H<sub>12</sub><sup>2-</sup> anion have been severely hampered until now by the fact that it could only be prepared in poor yield from a halogenated decaborane.<sup>2</sup> The high stability of this anion and of its derivatives, considered together with the versatility of its substitution reactions,<sup>3</sup> makes the chemistry of this ion an intriguing area for research. We would therefore like to report a more convenient preparation of this anion from readily available starting materials by conventional techniques. At the same time this is a striking example of the formation of a highly stable end product by a quite unexpected route. Small yields of B<sub>10</sub>H<sub>10</sub><sup>2-</sup> salts are produced as by-products.

In the course of carrying out <sup>11</sup>B n.m.r. spectral studies on the triborohydride anion it was found that heating a solution of NaB<sub>3</sub>H<sub>8</sub> in diethylene glycol dimethyl ether (141) for 2 hr. on a steam bath caused the <sup>11</sup>B n.m.r. spectrum to change. The multiplet arising from B<sub>3</sub>H<sub>8</sub><sup>-</sup> was completely replaced by a doublet of approximately the same over-all intensity with a chemical shift of 14.6 p.p.m. and a coupling constant of 126 c.p.s. This corresponded to the values for B<sub>11</sub>H<sub>14</sub><sup>-</sup> and B<sub>12</sub>H<sub>12</sub><sup>2-</sup> within experimental error.<sup>3,4</sup>

(1) Studies of Boranes IX. For paper VIII of this series see D. F. Gaines and R. Schaeffer, *Proc. Chem. Soc.*, 267 (1963).

(2) A. R. Pitochelli and M. F. Hawthorne, *J. Am. Chem. Soc.*, 82, 3228 (1960).

A freshly prepared solution of NaB<sub>3</sub>H<sub>8</sub> (18.5 g.) in 141 prepared by *in situ* hydroboration of sodium borohydride<sup>5</sup> was refluxed under a nitrogen atmosphere until colorless (16 hr.). When the resulting mixture was treated with a concentrated solution of (CH<sub>3</sub>)<sub>3</sub>NHCl (30 g.) in water an exothermic reaction occurred which was accompanied by evolution of gaseous amine. The resulting mixture was cooled to room temperature, and the solid which separated was filtered and dried to yield 27 g. of crude products.

A fraction of the crude solid was dissolved in water and treated with a saturated solution of cesium chloride in water until no further precipitation took place. The precipitate was recrystallized three times from water to give a highly crystalline colorless solid. An X-ray powder diffraction pattern of this solid showed maximum reflections at *d* values of 3.59, 4.21, 2.16, and 2.60 and was identical with the diffraction pattern of a similar material prepared in similar fashion from an authentic sample of (Et<sub>3</sub>NH)<sub>2</sub>B<sub>12</sub>H<sub>12</sub>.<sup>6</sup>

The remainder of the crude product was recrystallized from a water-ethanol mixture to give (Me<sub>3</sub>NH)<sub>2</sub>B<sub>12</sub>H<sub>12</sub> identified by its <sup>11</sup>B n.m.r. spectrum. Concentration of the mother liquor by conventional techniques gave further quantities of (Me<sub>3</sub>NH)<sub>2</sub>B<sub>12</sub>H<sub>12</sub> and also in the last fractions some (Me<sub>3</sub>NH)<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (identified by its <sup>11</sup>B n.m.r. spectrum).<sup>7</sup>

Yields were not definitely established, since complete separation of (Me<sub>3</sub>NH)<sub>2</sub>B<sub>12</sub>H<sub>12</sub> from (Me<sub>3</sub>NH)<sub>2</sub>B<sub>10</sub>H<sub>10</sub> could not be readily achieved, but the yield of B<sub>12</sub>H<sub>12</sub><sup>2-</sup> was at least 65%. The yield of B<sub>10</sub>H<sub>10</sub><sup>2-</sup> was roughly 3%.

Thin layer chromatography carried out on the crude reaction product using silica gel and water as eluent showed that it consisted of at least three components with respective R<sub>f</sub> values of 0, 0.3, and 1. The fraction with R<sub>f</sub> 1 was shown to be B<sub>12</sub>H<sub>12</sub><sup>2-</sup> and B<sub>10</sub>H<sub>10</sub><sup>2-</sup>. The other compounds present in the mixture are under investigation.

**Acknowledgment.**—The authors wish to thank Fred Tebbe for valuable discussions during this work. This work was supported by the Office of Naval Research.

(3) W. H. Knoth, *et al.*, *ibid.*, 84, 1056 (1962).

(4) V. D. Aftandilian, *et al.*, *Inorg. Chem.*, 1, 734 (1962).

(5) D. F. Gaines, R. Schaeffer, and F. Tebbe, *ibid.*, 2, 526 (1963).

(6) (Et<sub>3</sub>NH)<sub>2</sub>B<sub>12</sub>H<sub>12</sub> was kindly supplied by Professor M. F. Hawthorne.

(7) A. R. Pitochelli, *et al.*, *J. Am. Chem. Soc.*, 84, 1057 (1962).

CONTRIBUTION NO. 1159

DEPARTMENT OF CHEMISTRY  
INDIANA UNIVERSITY  
BLOOMINGTON, INDIANA

IAN A. ELLIS  
DONALD F. GAINES  
RILEY SCHAEFFER

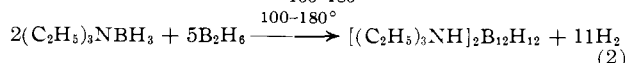
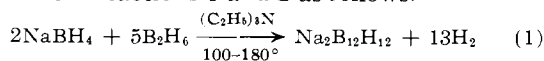
RECEIVED OCTOBER 4, 1963

### Synthesis of Polyhedral Boranes

Sir:

We wish to report a facile synthesis of polyhedral boranes, particularly B<sub>12</sub>H<sub>12</sub><sup>2-</sup>, directly from diborane.<sup>1</sup> The syntheses are based on two closely related reactions; (1) diborane and a metal borohydride, and (2) diborane and a base-borane complex. Other volatile boron hydrides may be used instead of diborane.

The B<sub>12</sub>H<sub>12</sub><sup>2-</sup> syntheses are the most important, and nearly quantitative yields of salts of B<sub>12</sub>H<sub>12</sub><sup>2-</sup> have been obtained from reactions 1 and 2 as follows.



In the second case, the triethylammonium salt is obtained directly in analytical purity. These reactions

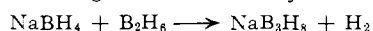
(1) (a) This ion was first reported by M. F. Hawthorne and A. R. Pitochelli, *J. Am. Chem. Soc.*, 82, 3228 (1960); (b) we are indebted to Professor R. Schaeffer, who advised us of the synthesis of B<sub>12</sub>H<sub>12</sub><sup>2-</sup> by pyrolysis of NaB<sub>3</sub>H<sub>8</sub> in diethylene glycol dimethyl ether: I. A. Ellis, D. F. Gaines, and R. Schaeffer, *ibid.*, 85, 3885 (1963).

TABLE I  
 POLYHEDRAL BORANE SYNTHESSES

Base-borane adduct	Temp., °C.	Products (% yield)
(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> NBH <sub>3</sub>	180	B <sub>12</sub> H <sub>12</sub> <sup>2-</sup> (>90)
(CH <sub>3</sub> ) <sub>3</sub> NBH <sub>3</sub>	175	B <sub>12</sub> H <sub>12</sub> <sup>2-</sup> (40-60), B <sub>12</sub> H <sub>11</sub> N(CH <sub>3</sub> ) <sub>3</sub> <sup>-</sup> (20), H <sub>2</sub> B[N(CH <sub>3</sub> ) <sub>3</sub> ] <sub>2</sub> <sup>+</sup> (8)
(CH <sub>3</sub> ) <sub>3</sub> PBH <sub>3</sub>	175	B <sub>12</sub> H <sub>12</sub> <sup>2-</sup> (low), B <sub>12</sub> H <sub>11</sub> P(CH <sub>3</sub> ) <sub>3</sub> <sup>-</sup> (60), H <sub>2</sub> B[P(CH <sub>3</sub> ) <sub>3</sub> ] <sub>2</sub> <sup>+</sup> (5)
(CH <sub>3</sub> ) <sub>3</sub> AsBH <sub>3</sub>	175	B <sub>12</sub> H <sub>11</sub> As(CH <sub>3</sub> ) <sub>3</sub> <sup>-</sup> (40), B <sub>12</sub> H <sub>10</sub> [As(CH <sub>3</sub> ) <sub>3</sub> ] (5), H <sub>2</sub> B[As(CH <sub>3</sub> ) <sub>3</sub> ] <sub>2</sub> <sup>+</sup> (4)
(CH <sub>3</sub> ) <sub>2</sub> SBH <sub>3</sub>	70	B <sub>11</sub> H <sub>14</sub> <sup>-</sup> (low), B <sub>9</sub> H <sub>13</sub> S(CH <sub>3</sub> ) <sub>2</sub> (low)
(CH <sub>3</sub> ) <sub>2</sub> SBH <sub>3</sub>	150	B <sub>12</sub> H <sub>12</sub> <sup>2-</sup> (1), B <sub>12</sub> H <sub>11</sub> S(CH <sub>3</sub> ) <sub>2</sub> <sup>-</sup> (20), B <sub>12</sub> H <sub>10</sub> [S(CH <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub> (30), H <sub>2</sub> B[S(CH <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub> <sup>+</sup> (2)

are best effected in sealed vessels. In place of diborane, B<sub>3</sub>H<sub>9</sub> has been used in reaction 1 and B<sub>6</sub>H<sub>9</sub>,<sup>†</sup> B<sub>10</sub>H<sub>14</sub>, and B<sub>18</sub>H<sub>22</sub> have been used in reaction 2. Other substitutions, *i.e.*, variations in solvent, base-borane complex, and temperature, lead to different products as noted below.

In dimethoxyethane rather than triethylamine, reaction 1 proceeds at 25° and 3 or more atmospheres of diborane pressure to give the triborohydride anion.



At 50° the yield of NaB<sub>3</sub>H<sub>8</sub> exceeds 90%. Above 50° with ethereal solvents, NaB<sub>11</sub>H<sub>14</sub> and Na<sub>2</sub>B<sub>12</sub>H<sub>12</sub> form in relative amounts that are dependent upon the particular ether employed. For example, in dimethoxyethane, the products at 120° are ~50% B<sub>12</sub> and 40% B<sub>11</sub>, whereas only B<sub>11</sub> forms in dioxane.

The products in reaction 2 are almost wholly dependent upon the nature of the base in the base-borane adduct. Replacement of triethylamine by a donor structure in which the donor atom is less hindered leads to the formation of B<sub>12</sub>H<sub>12</sub><sup>2-</sup> derivatives, *e.g.*, B<sub>12</sub>H<sub>11</sub>N(CH<sub>3</sub>)<sub>3</sub><sup>-</sup> and, in some cases, B<sub>9</sub>H<sub>14</sub><sup>-</sup> derivatives, *e.g.*, B<sub>9</sub>H<sub>13</sub>S(CH<sub>3</sub>)<sub>2</sub>. The use of less hindered bases also leads to the formation of cations of the type<sup>2</sup> H<sub>2</sub>B-(base)<sub>2</sub><sup>+</sup>. Representative results of reaction of B<sub>2</sub>H<sub>6</sub> with various base-borane adducts are listed in Table I. For simplicity, onium cations are not listed, only anions and borane cations.

In these borane syntheses, B<sub>3</sub>H<sub>8</sub><sup>-</sup> and possibly B<sub>3</sub>H<sub>7</sub><sup>-</sup> base appear to be important intermediates, and in fact, as noted above, moderate reaction temperature permits isolation of NaB<sub>3</sub>H<sub>8</sub> in high yield.<sup>3</sup> Furthermore, NaB<sub>3</sub>H<sub>8</sub> can be substituted for NaBH<sub>4</sub> in the synthesis of Na<sub>2</sub>B<sub>12</sub>H<sub>12</sub> and NaB<sub>11</sub>H<sub>14</sub>. Pentaborane(9) may also be an important intermediate. In reactions of diborane with trimethylamine, pentaborane(9) has been isolated at intermediate stages.

The new borane syntheses have no parallel in inorganic chemistry but are formally related to cracking reactions of neutral boranes and also of hydrocarbons. The simplicity of these syntheses and the high yields observed contrast sharply with the cracking reactions of neutral boranes. The difference may be a reflection of the facile formation of B<sub>3</sub>H<sub>8</sub><sup>-</sup> in our system as contrasted to the low, steady-state concentration of the presumed B<sub>3</sub>H<sub>7</sub><sup>-</sup> intermediate in the cracking of neutral boranes.

Chemical characterization of the novel derivatives of B<sub>12</sub>H<sub>12</sub><sup>2-</sup> in Table I will be the subject of a separate article.

(2) N. E. Miller and E. L. Muettterties, to be published.

(3) D. F. Gaines, R. Schaeffer, and F. Tebbe, *Inorg. Chem.*, **2**, 526 (1963), report a similar synthesis of NaB<sub>3</sub>H<sub>8</sub>.

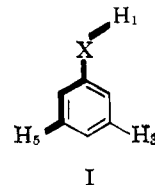
CONTRIBUTION No. 916  
 THE CENTRAL RESEARCH DEPARTMENT H. C. MILLER  
 EXPERIMENTAL STATION N. E. MILLER  
 E. I. DU PONT DE NEMOURS AND COMPANY E. L. MUETTERTIES  
 WILMINGTON 98, DELAWARE

RECEIVED OCTOBER 4, 1963

## Structural Studies by Nuclear Magnetic Resonance. VI. The Stereospecificity of Coupling between Protons Separated by Five Bonds and Conformations of Some Aromatic Aldehydes

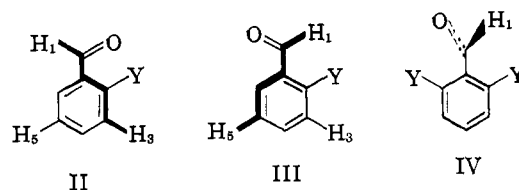
Sir:

In unsaturated systems proton couplings through five bonds are well documented.<sup>1</sup> When these systems are rigid<sup>1a,b,c,i</sup> the interacting protons are *trans-trans* coplanar. We wish to discuss system I, where X is an sp<sup>2</sup> hybridized carbon, nitrogen, or oxygen, and to point out, with emphasis on benzaldehydes, the dependence of *J*<sub>H<sub>1</sub>H<sub>5</sub></sub> on the dihedral angle formed by the H<sub>1</sub>XC and



XCH<sub>5</sub> planes.

We have examined at 60 Mc. the n.m.r. spectra of 65 benzaldehydes in several solvents and concentrations varying from neat to 5%. Table I summarizes a few representative data.<sup>2</sup> By varying Y, the carbonyl group can be forced to assume different conformations, *e.g.*, salicylaldehydes (Y = OH) have conformation II;



when Y = NO<sub>2</sub>, F, Cl, Br, OCH<sub>3</sub> the carbonyl group assumes conformation III.<sup>3</sup>

From the data we draw several conclusions: (a) H<sub>1</sub> couples only with hydrogens *meta* to the carbonyl group. (b) The coupling constant is independent of substituent electronic effects. (c) When the interacting protons are *trans-trans* coplanar (dihedral angle 180°), *e.g.*, H<sub>1</sub>-H<sub>3</sub> in II and H<sub>1</sub>-H<sub>5</sub> in III, the apparent coupling constant is about 0.7 c.p.s.; when they are *cis-trans* coplanar (dihedral angle 0°), *e.g.*, H<sub>2</sub>-H<sub>5</sub> in II and H<sub>1</sub>-H<sub>3</sub> in III, *J* = 0. Assuming that *para*-monosubstituted benzaldehydes are planar<sup>4</sup> with sufficiently fast flipping of the carbonyl group about the carbon-carbon single bond to make H<sub>3</sub> and H<sub>5</sub> equivalent, the apparent coupling should be the average of *trans-trans* and *cis-trans*. Indeed, for *para*-monosubstituted benzaldehydes H<sub>1</sub> is a triplet with spacings of 0.35 c.p.s. (d) For benzaldehydes substituted at both *ortho* positions, H<sub>1</sub> couples (triplet) with the hydrogens *meta* to the carbonyl with *J* = 0.35 c.p.s. If in these compounds the

(1) (a) J. E. Elvidge and R. G. Foster, *J. Chem. Soc.*, 590 (1963); (b) F. A. L. Anet, *J. Chem. Phys.*, **32**, 1274 (1960); (c) R. J. Tuite, H. R. Snyder, A. L. Porte, and H. S. Gutowsky, *ibid.*, **35**, 187 (1961); (d) J. B. Leane and R. E. Richards, *Trans. Faraday Soc.*, **55**, 518 (1959); (e) S. Gronowitz and R. A. Hoffman, *Acta Chem. Scand.*, **13**, 1687 (1959); (f) V. J. Kowalewski and D. G. de Kowalewski, *J. Chem. Phys.*, **36**, 266 (1962); (g) T. Schaefer, *ibid.*, **36**, 2235 (1962); (h) J. A. Elvidge and L. M. Jackman, *Proc. Chem. Soc.*, 89 (1959); (i) G. J. Karabatsos, B. L. Shapiro, F. M. Vane, J. S. Fleming, and S. Ratka, *J. Am. Chem. Soc.*, **85**, 2784 (1963); (j) R. Freeman, N. S. Bhacca, and C. A. Reilly, *J. Chem. Phys.*, **38**, 293 (1963).

(2) *J* values were computed from first-order analysis with reasonably good first-order spectra being obtained for most disubstituted and trisubstituted benzaldehydes. For monosubstituted benzaldehydes, especially *ortho* and *meta*, the complex aromatic region (ABCDX systems) was usually not analyzed and *J* values were computed from the first-order appearance of the H<sub>1</sub> doublet. In all cases δ(H<sub>1</sub>H<sub>3</sub>)/*J*<sub>H<sub>1</sub>H<sub>3</sub></sub> = 200-500.

(3) The conformation of *o*-nitrobenzaldehyde has been shown to be III; see K. E. Calderbank and R. J. W. LeFèvre, *J. Chem. Soc.*, 1463 (1949).

(4) Benzaldehyde is planar according to R. Bramley and R. J. W. LeFèvre, *ibid.*, 58 (1962).