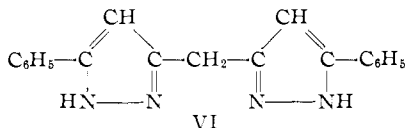


I showed, in addition to peaks corresponding to the methylene and vinyl hydrogens, three peaks with chemical shifts of 2.02, 2.05, and 2.30 p.p.m. which were assigned to the terminal methyl protons.<sup>5</sup>

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., 310. 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

RECEIVED NOVEMBER 2, 1963

### 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

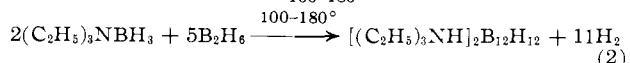
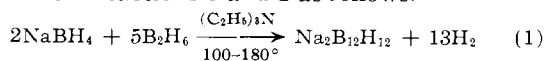
RECEIVED OCTOBER 4, 1963

### 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).