

The hydroxyl groups at C-11 and C-15 are recognized as broad bands within the range 5.6–7.0  $\tau$ , which shift on dilution. The carbon bonded hydrogens in these positions appear between 5.6 and 6.2  $\tau$  and the protons of the carbomethoxy group are superimposed on this region with a sharp peak at 4.37  $\tau$ . The n.m.r. spectra of PGE<sub>1</sub> and PGE<sub>2</sub> exhibit essentially the same absorption pattern at these frequencies.

Of particular interest is the absorption due to the protons of the methyl group (C-20) which appears as a clear triplet at 9.05  $\tau$  and with a coupling constant of 7 c.p.s., whereas corresponding groups in PGE<sub>1</sub> and PGE<sub>2</sub> appear as relatively sharp peaks at 9.10  $\tau$  flanked by broad bands. The spin-spin splitting and chemical shift of the methyl protons in PGE<sub>3</sub> demonstrate that the double bond in the terminal pentyl group is located between C-17 and C-18. The same pattern for the methyl protons has been observed for methyl linolenate,<sup>5</sup> methyl densipolate<sup>6</sup> and other fatty acids containing a double bond in  $\beta,\gamma$ -position to the terminal methyl group.<sup>5</sup>

The data also exclude the presence of a double bond between C-16 and C-17 or between C-18 and C-19. In the former case the olefinic protons would appear at lower frequency due to the hydroxyl group at C-15, and in the latter case the methyl protons would appear as a doublet at lower frequency. The structure of prostaglandin E<sub>3</sub> (11 $\alpha$ ,15-dihydroxy-9-keto-prosta-5,13,17-trienoic acid) is shown in Fig. 1.

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(6) C. R. Smith, Jr., T. L. Wilson, R. B. Bates and C. R. Scholfield, *J. Org. Chem.*, **27**, 3112 (1962).

DEPARTMENT OF CHEMISTRY  
KAROLINSKA INSTITUTET  
STOCKHOLM, SWEDEN

BENGT SAMUELSSON

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### The Molecular Structure of *i*-B<sub>18</sub>H<sub>22</sub>

Sir:

We have established by three dimensional X-ray diffraction methods the chemical composition and molecular structure of a new boron hydride, *i*-B<sub>18</sub>H<sub>22</sub>. This is the first example of isomers among the known boron hydrides. The relation of the structure of *i*-B<sub>18</sub>H<sub>22</sub> to the previously described<sup>1</sup> B<sub>18</sub>H<sub>22</sub> structure is shown as I and II, respectively, in Fig. 1.

*i*-B<sub>18</sub>H<sub>22</sub> appears as a lesser product of the reaction<sup>2</sup> which produces B<sub>18</sub>H<sub>22</sub> from the B<sub>20</sub>H<sub>18</sub><sup>-2</sup> ion.<sup>3</sup> A total of 3206 independent X-ray diffraction maxima were obtained from about 10,000 observations on single crystals. The unit cell is monoclinic, of symmetry P2<sub>1</sub>/c, and has parameters  $a = 9.199 \pm 0.002$ ,  $b = 13.180 \pm 0.001$ ,  $c = 12.515 \pm 0.002$  and  $\beta = 109^\circ 35'$ . The measured density of 1.003 g./cm.<sup>3</sup> requires four molecules per unit cell and yields the calculated molecular weight 215.7 in good agreement with the value 216.8 for the formula B<sub>18</sub>H<sub>22</sub>. Aside from anisotropic thermal parameters for B, isotropic thermal parameters for H and a single scale factor, there are 54 position parameters for B and 66 position parameters for H which were then determined by the 3206 observations.

The boron arrangement was solved by simultaneous multiple superposition procedures<sup>4,5</sup> following a detailed

(1) P. G. Simpson and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U.S.A.*, **48**, 1490 (1962); *J. Chem. Phys.*, in press.

(2) A. R. Pitochelli and M. F. Hawthorne, *J. Am. Chem. Soc.*, **84**, 3218 (1962).

(3) A. Kaczmarczyk, R. D. Dobrott and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U.S.A.*, **48**, 729 (1962).

(4) P. G. Simpson and W. N. Lipscomb, Abstracts, American Crystallographic Association Meeting, Cambridge, Massachusetts, April 28–30.

(5) P. G. Simpson, R. D. Dobrott and W. N. Lipscomb, to be published.

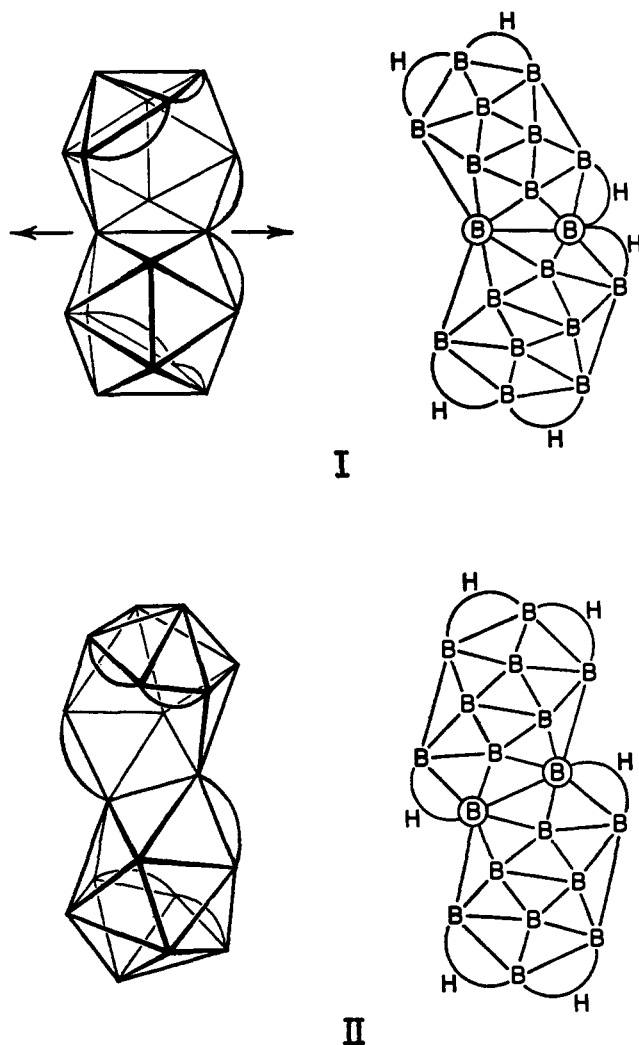


Fig. 1.—Comparison of structures of *i*-B<sub>18</sub>H<sub>22</sub> (I) and B<sub>18</sub>H<sub>22</sub> (II). The former has a twofold axis indicated by arrows, whereas the latter has a center of symmetry. One terminal H atom has been omitted from each B atom except for the encircled B atoms which do not have terminal H atoms. The two bridge H atoms to the circled B in I are considerably above and below the plane of the drawing, and hence do not present a steric problem. The most positively charged B atom is the circled B atom attached to two bridge H atoms in I.

analysis of the symmetry minimum function<sup>5</sup> derived from the sharpened three-dimensional Patterson function. No assumptions were made about the number or positions of the H atoms all of which were located uniquely from three-dimensional electron density maps from which the B atoms had been subtracted. Thus these methods also provide a determination of the chemical formula. At the present state of refinement the value of  $R = \sum ||F_0| - |F_c|| / \sum |F_0|$  is 0.10 for all observed reflections.

The structures of *i*-B<sub>18</sub>H<sub>22</sub> and B<sub>18</sub>H<sub>22</sub> (Fig. 1) may be described as decaborane-14 cages joined by atoms in common at the 5–6 positions (the circled B atoms) in such a manner that the cages open up in opposite directions. The manner of joining is 5 in common with 5' (*i.e.*, 5–5') and 6–6' in *i*-B<sub>18</sub>H<sub>22</sub>, which has a twofold axis of symmetry, and 5–6' and 6–5' in B<sub>18</sub>H<sub>22</sub>, which has a center of symmetry. Each of the B atoms except those which are circled has a terminal H atom, which is not shown in the diagram.

A theoretical study of the charge distribution in *i*-B<sub>18</sub>H<sub>22</sub> is being undertaken in order to provide a basis for prediction of its nucleophilic and electrophilic

chemistry. This structure extends the list of structurally characterized boron hydrides to include  $B_2H_6$ ,  $B_4H_{10}$ ,  $B_5H_9$ ,  $B_6H_{11}$ ,  $B_6H_{10}$ ,  $B_9H_{15}$ ,  $B_{10}H_{14}$ ,  $B_{10}H_{16}$ ,  $B_{18}H_{22}$  and *i*- $B_{18}H_{22}$ .

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DEPARTMENT OF CHEMISTRY  
HARVARD UNIVERSITY  
CAMBRIDGE, MASSACHUSETTS

PAUL G. SIMPSON  
KIRSTEN FOLTING  
WILLIAM N. LIPSCOMB

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### Tricyclo[2.1.1.0<sup>5,6</sup>]hexane-5-*t*-butylcarboxamide: Synthesis and Carbanion Formation<sup>1</sup>

Sir:

Several years ago we described the n.m.r. spectrum of *exo*-5-chlorobicyclo[2.1.1]hexane-*exo*-6-*t*-butylcarboxamide (Ia), which exhibited a dramatic long range spin-spin coupling ( $J = 7$  c.p.s.) between the distant *endo* C-5 and C-6 protons.<sup>2</sup> We now wish to report a

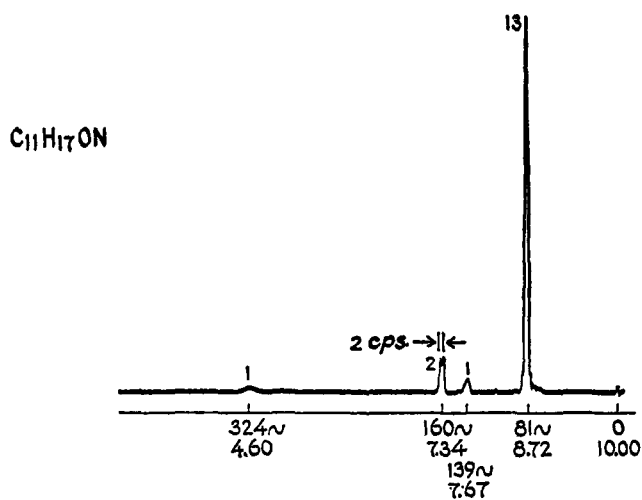
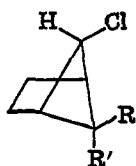


Fig. 1.—N.m.r. spectrum, 60 Mc., ( $CDCl_3$  solution) of  $C_{11}H_{17}ON$  (numbers over peaks give relative areas; peak positions are given relative to tetramethylsilane in c.p.s. and  $\tau$ ).

novel dehydrohalogenation of Ia to a system forming a new type of carbanion. Treatment of Ia with excess *n*-butyllithium followed by quenching with water yielded a saturated crystalline product,  $C_{11}H_{17}ON$ ,<sup>3</sup> m.p. 159.5–160.0°, whose infrared and n.m.r. (see Fig. 1) spectra showed the *t*-butylcarboxamide function to be still intact [infrared max. ( $CCl_4$ ), N—H, 2.95  $\mu$ ; C=O, 6.00  $\mu$ ].



- Ia. R = CONHC(CH<sub>3</sub>)<sub>3</sub>; R' = H  
Ib. R = H; R' = CONHC(CH<sub>3</sub>)<sub>3</sub>  
Ic. R = CONHC(CH<sub>3</sub>)<sub>3</sub>; R' = D

(Analogous treatment of the epimeric *exo*-5-chlorobicyclo[2.1.1]hexane-*endo*-6-*t*-butylcarboxamide (Ib)

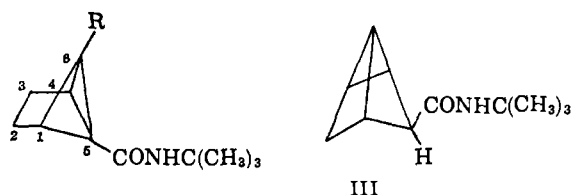
(1) The support of this work by research grants from the National Science Foundation and the National Institutes of Health is acknowledged with pleasure.

(2) J. Meinwald and A. Lewis, *J. Am. Chem. Soc.*, **83**, 2769 (1961); W. D. Kumler, A. Lewis and J. Meinwald, *ibid.*, **83**, 4591 (1961).

(3) Satisfactory analytical data have been obtained for these new compounds.

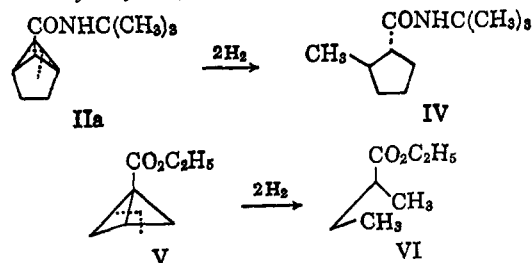
with *n*-butyllithium or even *t*-butyllithium yielded only starting material.)

These data require a tricyclic structure, the two most likely possibilities being IIa and III. The relatively simple n.m.r. spectrum (Fig. 1) favors the more symmetrical structure IIa, since III has no two of its skeletal protons equivalent.



- IIa. R = H    IIc. R = CH<sub>3</sub>  
IIb. R = D    IIe. R = CO<sub>2</sub>H  
                  IIe. R = CO<sub>2</sub>CH<sub>3</sub>

Chemical evidence supporting structure IIa was provided by hydrogenolysis which yielded, after the uptake of two moles of hydrogen, *trans*-2-methylcyclopentane-*t*-butylcarboxamide (IV)<sup>3</sup> identified by direct comparison with an authentic sample.<sup>4</sup> That both moles of hydrogen were absorbed simultaneously, or in rapid succession, was shown by the absence of the possible dihydro compounds (which have been synthesized) in partially hydrogenated samples. The course of hydrogenolysis is closely analogous to that of 1-carboethoxybicyclo[1.1.0]butane<sup>5</sup> (V → VI).



Structure III does not appear compatible with the formation of this hydrogenolysis product, since the required reductive cleavage of a carbon-carbon bond which is not part of a three-membered ring lacks analogy. Further chemical evidence in favor of structure IIa is not available, as attempts to hydrolyze the *t*-butylamide function without destroying the ring system have been unsuccessful.

In studying the mechanism of the novel cyclization of Ia, it became desirable to investigate the behavior of the analogous deuterated compound Ic.<sup>2</sup> Following the procedure previously described, the product IIa was found to have lost its deuterium. However, when either Ia or Ic was cyclized with *n*-butyllithium and quenched with  $D_2O$ , the 6-deuterio product IIb was obtained. The same product was obtained by treatment of IIa itself with *n*-butyllithium, followed by  $D_2O$ . The n.m.r. spectrum of IIb shows exactly the expected relationship to that of IIa, and provides excellent support for the proposed structures. Thus, the unresolved multiplet assigned to the C-6 proton (7.67  $\tau$ ) vanishes, and the doublet assigned to the C-1 and C-4 protons (7.34  $\tau$ ) (previously split by the C-6 proton) becomes a singlet.

These results lead to the surprising conclusion that the proton on C-6 is sufficiently acidic to be removed by *n*-butyllithium. Further diagnostic reactions of the anion were obtained by quenching the reaction mixture with methyl iodide to give the methylated product IIc,

(4) An authentic sample of *trans*-2-methylcyclopentane carboxylic acid was made available to us by Prof. J. R. Johnson and Mr. E. Raleigh of these laboratories.

(5) K. B. Wiberg and R. P. Ciula, *J. Am. Chem. Soc.*, **81**, 5261 (1959).