

Fig. 1.—The quasi-planar ring skeleton of one PyrVal<sup>-</sup> chelated to Mn<sup>++</sup>. Bond lengths and angles are as shown; the sum of the interior angles in each ring appears at the ring center. The pyridine ring, including all directly attached atoms, is essentially flat; the other rings, which include Mn(II), are necessarily somewhat folded and twisted (see text). Bond lengths (with standard deviations mostly >0.015 Å.) are generally compatible with the model postulated by earlier workers.

complexes which have received attention as model substances for the transaminase enzyme systems.<sup>2-5</sup> Christensen's appraisal<sup>4</sup> of the stereochemical possibilities open to these complexes poses several rather fundamental questions which we have undertaken to answer through X-ray analysis of crystalline structure. Preliminary results are reported herein for the manganese(II) chelate of pyridoxylidenevaline, Mn(Pyr-Val)<sub>2</sub>, prepared following Christensen<sup>4</sup> except for the use of D,L-valine instead of L-valine as a starting material<sup>6</sup>; the special virtue of this preparation was to furnish crystals usable for structure determination.

The Mn(II) chelate crystallizes in the space group *Pcan* with  $a = 9.15 \pm 0.02$ ,  $b = 16.84 \pm 0.01$ ,  $c = 19.765 \pm 0.01$  Å. The unit cell contains 4Mn(Pyr-Val)<sub>2</sub> and, in principle, 16H<sub>2</sub>O (one set of eight fold positions is incompletely filled). Three-dimensional

(2) D. E. Metzler, M. Ikawa and E. E. Snell, *J. Am. Chem. Soc.*, **76**, 648 (1954).

(3) J. B. Longenecker and E. E. Snell, *ibid.*, **79**, 142 (1957).

(4) H. N. Christensen, *ibid.*, **79**, 4073 (1957).

(5) E. E. Snell and W. T. Jenkins, *J. Cellular Comp. Physiol.*, **54**, Supplement, 161 (1959).

(6) The use of L-valine gave crystals of the Mn(II), Cu(II), and Fe(III) chelates agreeing closely with Christensen's description of his products, of which none was usable for structure determination; the Fe(III) chelate, for example, displayed an astonishing internal disorder. The use of D,L-valine gave crystals of the Mn(II) and Cu(II) chelates which, at least superficially, were very different from those obtained with L-valine. These unanticipated observations suggest incomplete racemization of the amino acid prior to crystallization of the chelate, and are to receive further study.

intensity data from a crystal plate having about one-tenth of the optimum volume wanted with MoK $\alpha$  radiation in the technique described earlier<sup>7</sup> were counter-recorded for the range,  $(\sin\theta)/\lambda < 0.65$ . Some 1100 independent  $\{hkl\}$ , about 40% of normal expectancy, were measurable above background; the use of an alternative radiation was impracticable for various reasons. The intensity data sufficed, nonetheless, for structure determination by Patterson and Fourier methods to give results which are qualitatively certain and quantitatively illuminating. At a late stage of refinement, with use of anisotropic thermal parameters for individual atoms, the conventional *R* is 0.10 for the 1100 observable  $\{hkl\}$  amplitudes. The more pertinent bond parameters of the molecule are shown on Fig. 1.

Octahedral coordination for manganese is achieved with the one pattern (apart from its enantiomorph) which can allow essential planarity of the fused ring systems; a twofold axis bisecting opposite pairs of octahedral edges renders the two PyrVal<sup>-</sup> of a molecule structurally equivalent. The distortion from planarity in the ring skeleton of a PyrVal<sup>-</sup> chelated to the excessively large Mn<sup>++</sup> is bound to be significant, with the detailed pattern determined in part by packing relations in the crystal. A bowing of the fused ring system along its principal axis and a rather more important twisting about this axis combine to give a dihedral angle of roughly 150° between the mean planes of the pyridine and valinate rings. Of interest in this connection is the following intermolecular hydrogen bonding: carboxylate oxygen to pyridine nitrogen at 2.68 Å., the second carboxylate oxygen to a water molecule at 2.69 Å., and this same water molecule to methanolic oxygens of two complexes at 2.65 and 2.74 Å. It is readily calculable that the use of cations small enough to give complexing bonds averaging <2.0 Å. would go far toward minimizing ring strain in a chelated Pyr-Val<sup>-</sup>.

Christensen's studies<sup>4</sup> led him to postulate especially weak complexing of phenolic oxygen to M(II) ions (excepting Cu(II) in the 1:1 chelate), but our data (Fig. 1) lead to precisely the opposite conclusion. Although detailed correlations with bonding theory must await a full report, our stereochemical data seem generally to qualify the chelate type of Fig. 1 for the postulated role of catalytic intermediate in the reactions of interest.<sup>2,3,5</sup> We hope to learn more about the disconcerting behavior of these systems during crystallization,<sup>6</sup> and to obtain internally well ordered crystals suitable for the authoritative evaluation of bond parameters.

(7) J. V. Silverton and J. L. Hoard, *Inorg. Chem.*, **2**, 243 (1963).

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#### BON-BON, A NOVEL 6-MEMBERED HETEROCYCLE CONTAINING BORON, OXYGEN AND NITROGEN

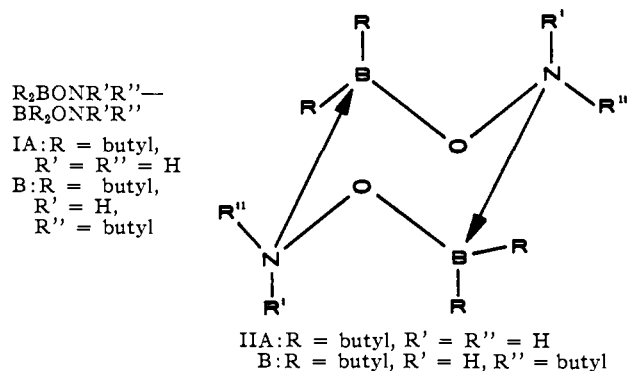
Sir:

In a study of the reaction between nitric oxide and tri-*n*-butyl-borane which will be described elsewhere, we have obtained some new boron compounds which, upon hydrolysis, yield di-*n*-butylborinic acid and *N-n*-butyl-hydroxylamines. It is the purpose of this communication to describe the synthesis and characterization of these compounds.

The addition of an alcoholic solution of hydroxylamine to di-*n*-butylborinic acid results in the immediate

formation of a crystalline solid whose analysis after recrystallization from ether is compatible with the formulation  $R_2BONH_2$ , (aminoöxy) di-*n*-butylborane (*Anal.* Calcd. for  $C_8H_{20}BON$ : C, 61.22; H, 12.75; N, 8.93; B, 6.89. Found: C, 61.44; H, 12.70; N, 8.89; B, 6.92); decomposes before melting at  $130^\circ$ .

Molecular weight determination of this substance in acetonitrile solution, concentration = 0.05 formal, at  $35^\circ$ , made with a Mechrolab osmometer indicates that it is dimeric (molecular weight of dimer, calcd.: 314, found:  $300 \pm 20$ ). The dimer may be either acyclic, having the structure IA, or cyclic, having the structure IIA.



These two structures are distinguishable on the basis of their N-H bands. Structure I should have two pairs of N-H bands. The pair being due to the symmetric and antisymmetric stretching of the hydrogens on the tetracoordinated nitrogen should be found at 3200 to 3300  $cm^{-1}$ , and the pair being due to the symmetric and antisymmetric stretching of the hydrogens on the trivalent nitrogen should occur at 3400 to 3500  $cm^{-1}$ . Structure II should have only one pair of N-H bands and they should occur at 3200 to 3300  $cm^{-1}$  since both nitrogens are equivalent and are tetracoordinated. The infrared spectrum of a dilute solution of (aminoöxy) di-*n*-butylborane in  $CCl_4$  (concn. = 0.05 *M*, cell thickness = 1 cm.) shows only one pair of N-H bands which are at 3310 and 3270  $cm^{-1}$ , indicating the cyclic structure, IIA, is correct.

Reaction of *N*-*n*-butylhydroxylamine with di-*n*-butylborinic acid yields crystalline (*N*-butylaminoöxy) di-*n*-butylborane,  $R_2BONHR$ , m.p.  $92-94^\circ$ . (*Anal.* Calcd. for  $C_{12}H_{28}BON$ : C, 67.60; H, 13.14; N, 6.57; B, 5.07. Found: C, 67.69; H, 13.28; N, 6.62; B, 5.37.) Molecular weight of this compound in benzene solution showed that it too is dimeric (calcd. for dimer: 426; found: 404, by freezing point depression, and  $415 \pm 15$  by osmometry). The infrared spectrum of a dilute solution in  $CCl_4$  shows a single N-H band at 3210  $cm^{-1}$  indicating the cyclic structure IIB. We propose the name Bon-Bon for this novel heterocycle represented by II. The 1,1,4,4-tetrasubstituted bon-bons which are formed by the reaction of borinic acids with hydroxylamine can be used to advantage as solid derivatives of borinic acids, since they form readily, they are stable in air (borinic acids oxidize quickly in air) and they are easily recrystallized from organic solvents.

The reaction between *N,N*-di-*n*-butylhydroxylamine and dibutylborinic acid yields the liquid product, (*N,N*-dibutylaminoöxy) dibutylborane,  $R_2BONR_2$ , b.p.  $78^\circ$  (2.5 mm.) Our product was slightly contaminated by di-*n*-butylborinic acid as evidenced by the weak OH band at 3627  $cm^{-1}$  which is characteristic for borinic acids in  $CCl_4$  solution (*Anal.* Calcd. for  $C_{16}H_{36}BON$ :

C, 71.37; H, 13.38; N, 5.20; B, 4.01. Found: C 71.60; H, 12.64; N, 4.89; B, 3.97.)

This compound, in contrast to the two previously described derivatives, is monomeric in 0.05 formal benzene solution (molecular weight for monomer, calcd.: 269; found:  $230 \pm 20$ ). If this compound had the bon-bon structure it would have two axial butyl groups at positions 1 and 3, and two more at positions 4 and 6. Apparently the steric interference between the two pairs of axial butyl groups prevents the cyclic structure from forming and at the same time reduces the tendency to dimerize. In IIA and IIB there are no axial-axial interactions between butyl groups.

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#### THE REACTIONS OF SULFUR ATOMS. II. SULFUR ATOM INSERTION IN CARBON-HYDROGEN BONDS. THE FORMATION OF CYCLOPROPYL MERCAPTAN IN THE REACTION WITH CYCLOPROPANE

Sir:

Recent investigations in this Laboratory on the reactions of S-atoms with olefins<sup>1</sup> are currently being extended to include paraffinic hydrocarbons. Here evidence has been found for the first time that sulfur atoms, in the (<sup>1</sup>D) state from the photolysis of gaseous carbonyl sulfide, undergo an insertion reaction into carbon-hydrogen bonds. While a quantitative kinetic treatment of a series of such substrates<sup>2</sup> will be forthcoming shortly, the results obtained with cyclopropane are being reported here since they are illustrative of the general behavior of the sulfur atom-paraffin systems under investigation. In addition, the present reaction is of special interest in that the expected isomerization of the cyclopropyl compound to the allyl isomer does not occur. Finally, the insertion reaction represents a relatively simple method for preparing cyclopropyl and other mercaptans from the corresponding paraffins.

When carbonyl sulfide and cyclopropane, at partial pressures of 50–300 and 70–1100 mm., respectively, were irradiated in a static system at  $25^\circ$ , in the wave length region 2290–2550 Å., using a suitably filtered mercury arc, the major products were CO, sulfur, and cyclopropyl mercaptan. Carbon monoxide was removed by pumping at  $-196^\circ$ , while unreacted COS and cyclopropane were removed by distillation at  $-130^\circ$ . The remaining fraction, analyzed by gas chromatography on an 8-ft. 15% silicone 550 (with 2% stearic acid) on Celite column at  $25^\circ$  with  $H_2$  carrier at 65 ml./min., was found to be at least 95% cyclopropyl mercaptan. The remainder was  $CS_2$  and a trace of unknown. Identification analyses were performed on mercaptan samples trapped from the chromatographic effluent.

The identity of the mercaptan was confirmed by mass spectrometric, infrared and n.m.r. analysis. The mass spectrum showed a molecular weight of 74, and the infrared spectrum was consistent with that expected for cyclopropyl mercaptan. The n.m.r. spectrum exhibited four complex multiplets centered on  $\tau$  values of A, 8.05; B, 8.23; C, 9.26; and D, 9.53; with integrated areas being in the ratio 1:1:2:2. Peaks C and D may be assigned to the methylene protons on the cyclopropyl ring since the occurrence of such signals at high fields has been observed for cyclopropylamine and methyl cyclopropyl carboxylate.<sup>3</sup> Peak B resembles that observed for the methine proton in the

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(2) A. R. Knight, O. P. Strausz and H. E. Gunning, to be published.

(3) Varian Associates, "N.M.R. Spectra Catalog," Palo Alto, California, 1962.