

This communication presents results from reinvestigating once more the nitrous acid deamination of I-1-<sup>14</sup>C.

I-1-<sup>14</sup>C was prepared from potassium <sup>14</sup>C-cyanide and deaminated by nitrous acid in aqueous perchloric acid as described by Roberts and Halmann.<sup>2</sup> The 1-propanol fraction was isolated by preparative v.p.c. Degradation was effected according to the procedures of Reutov and Shatkina,<sup>3</sup> involving oxidation of the 1-propanol to propionic acid and then to acetic acid followed by conversion of the latter to methylamine *via* the Schmidt reaction. The propionic and acetic acids were converted to the corresponding *p*-bromophenacyl esters and the methylamine was converted to N-methyl-*p*-toluenesulfonamide. The radiochemical purity of these solid derivatives was assured by repeated recrystallizations until their specific activities were constant. The data on the rearrangements of <sup>14</sup>C are summarized in Table I.

Table I. Activity Data and Rearrangements of the <sup>14</sup>C-Label in the 1-Propanol from Deamination of 1-<sup>14</sup>C-1-Propylammonium Perchlorate

Compd. Assayed	Specific activity, <sup>a</sup> c.p.m./mmole		% <sup>14</sup> C in C-2 and C-3		% <sup>14</sup> C in C-3	
	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2
CH <sub>3</sub> CH <sub>2</sub> COOH <sup>b</sup>	7340	194,700				
CH <sub>3</sub> COOH <sup>b</sup>	297	8,030	4.1	4.1		
CH <sub>3</sub> NH <sub>2</sub> <sup>c</sup>	109	3,600			1.5	1.9

<sup>a</sup> Measured by a liquid scintillation counter. <sup>b</sup> Assayed as the *p*-bromophenacyl ester. <sup>c</sup> Assayed as N-methyl-*p*-toluenesulfonamide.

Of the two runs summarized in Table I, data from run 2 are likely more reliable because of the higher activities. The results indicate a total of about 4% rearrangement, with the rearranged <sup>14</sup>C approaching equal distribution in C-2 and C-3. This distribution is in very close agreement with that predicted by Karabatsos and co-workers<sup>6</sup> on the basis of their results from studies of deaminations of 1,1-dideuterio-1-propylammonium perchlorate (I-1-*d*<sub>2</sub>) and 2,2-dideuterio-1-propylammonium perchlorate (I-2-*d*<sub>2</sub>) by mass spectroscopy. The difference between the presently observed total rearrangement of 4% from the earlier reported 8% possibly may be due, at least in part, to inadequate purification of the compounds assayed by the previous workers.<sup>2,3</sup> In the course of the present work it was noted that apparently higher activity contents were observed if the solid derivatives of the degradation products were not repeatedly recrystallized until the specific activities were constant.

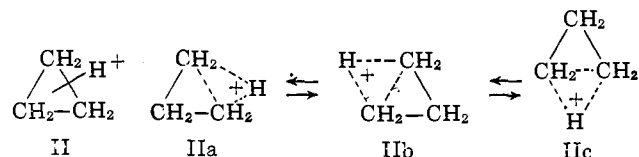
The finding of almost equal distribution of the rearranged <sup>14</sup>C in C-2 and C-3, together with the results from deaminations of I-1-*t* and I-2-*d*<sub>2</sub> recorded in the previous communication,<sup>4</sup> clearly support the involvement of protonated cyclopropane (II) as an intermediate or a transition state in giving rise to the isotopic rearrangements observed in the 1-propanol. A completely symmetrical protonated cyclopropane was first suggested in 1960 by Skell and Starer,<sup>7</sup> although these workers later preferred the 1,3-hydride shift.<sup>8</sup> The pre-

(6) G. J. Karabatsos, C. E., Orzech, Jr., and S. Meyerson, private communications.

(7) P. S. Skell and I. Starer, *J. Am. Chem. Soc.*, **82**, 2971 (1960).

(8) P. S. Skell and I. Starer, *ibid.*, **84**, 3962 (1962).

sent data and those of Baird<sup>5</sup> and Karabatsos<sup>6</sup> suggest a situation where the three carbon positions are equivalent or approaching equivalence. The experimental results, however, do not differentiate between "face-protonated" (II) and "edge-protonated" (IIa-c) cyclopropanes.



From the present work and others already reported in the literature, it may be concluded that the 1-propyl cation from deamination of 1-propylamine may react with solvent to give 1-propanol, deprotonate to propene, undergo irreversible 1,2-hydride shift leading to 2-propanol, and cyclize to II which may deprotonate to cyclopropane or collapse to give isotopically rearranged 1-propanol. The results from deamination of I-1-*t*<sup>4</sup> and I-1-<sup>14</sup>C indicate a total of about 3-4% isotopic rearrangements from C-1 to C-2 and C-3, which means that about 4-6% of the 1-propanol obtained in the deamination is derived from protonated cyclopropane.

(9) Holder of a Canadian Industries Ltd. Fellowship, 1963-1964, and a Canadian Chemicals Ltd. Fellowship, 1964-1965.

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### Carbametallic Boron Hydride Derivatives. III. The $\pi$ -C<sub>5</sub>H<sub>5</sub>Fe( $\pi$ -B<sub>9</sub>C<sub>2</sub>H<sub>11</sub>) System

Sir:

In the first communication of this series<sup>1</sup> we reported the synthesis of (B<sub>9</sub>C<sub>2</sub>H<sub>11</sub>)<sub>2</sub>Fe<sup>-</sup> (I) and (B<sub>9</sub>C<sub>2</sub>H<sub>11</sub>)<sub>2</sub>Fe<sup>-2</sup> (II). Evidence available at that time suggested the possibility of "sandwich" bonding between each B<sub>9</sub>C<sub>2</sub>H<sub>11</sub><sup>-2</sup> ion<sup>1</sup> (III) and Fe<sup>II</sup> and Fe<sup>III</sup>. A more recent report<sup>2</sup> was concerned with probable analogs of  $\pi$ -C<sub>5</sub>H<sub>5</sub>M(CO)<sub>3</sub>; (B<sub>9</sub>C<sub>2</sub>H<sub>11</sub>)M(CO)<sub>3</sub><sup>-</sup> (IV) where M = Mn and Re. We now wish to report the preparation and properties of  $\pi$ -C<sub>5</sub>H<sub>5</sub>Fe( $\pi$ -B<sub>9</sub>C<sub>2</sub>H<sub>11</sub>) containing Fe<sup>II</sup> (V) and Fe<sup>III</sup> (VI) which appears to be analogous to the ferrocene-ferricinium ion system. The accompanying communication<sup>3</sup> describes the single crystal X-ray diffraction study which confirms the "sandwich" structure of VI.<sup>4</sup>

(1) M. F. Hawthorne, D. C. Young, and P. A. Wegner, *J. Am. Chem. Soc.*, **87**, 1818 (1965).

(2) M. F. Hawthorne and T. D. Andrews, *ibid.*, **87**, 2496 (1965).

(3) A. Zalkin, D. H. Templeton, and T. E. Hopkins, *ibid.*, **87**, 3988 (1965).

(4) Existing nomenclature systems are not capable of generating reasonably brief names for compounds such as I, II, IV, V, and VI. Accordingly, we suggest that the parent B<sub>11</sub>H<sub>11</sub><sup>-4</sup> ion, which is isoelectronic with the isomeric series of B<sub>9</sub>C<sub>2</sub>H<sub>11</sub><sup>-2</sup> ions, be called ollide ion after the Spanish noun, *olla* (jar or kettle). The isomeric B<sub>9</sub>C<sub>2</sub>H<sub>11</sub><sup>-2</sup> ions would then become (1)-2,3-dicarbollyl ion, etc., where the number in parentheses denotes the position of the missing BH unit which generates the "hole" in the icosahedron. The prefix  $\pi$ - or  $\sigma$ - would be employed to denote the mode of attachment of the (1)-2,3-dicarbollyl, etc., group to other atoms. Thus, VI becomes  $\pi$ -cyclopentadienyl- $\pi$ -(1)-2,3-dicarbollyliron(III). The use of  $\pi$ - and  $\sigma$ -terminology rests upon the obvious geometrical analogy found in organometallic compounds. The actual bonding arrangement in the so-called  $\pi$ -derivatives remains as an open question which is under examination.

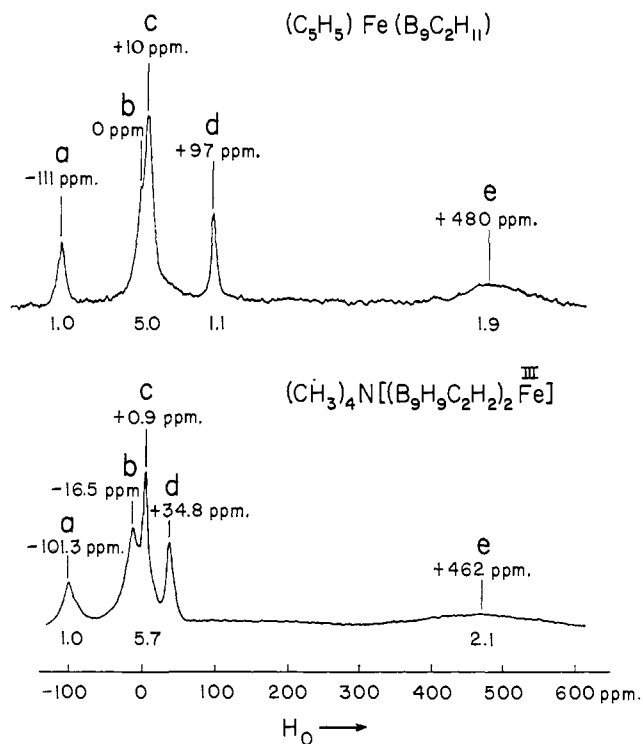


Figure 1. The 19.3-Mc./sec.  $^{11}\text{B}$  n.m.r. spectra of VI and tetramethylammonium I determined in tetrahydrofuran and acetonitrile, respectively, with  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  standard.

Compound VI was obtained in the following manner. A solution of 20 mmoles each of disodium (1)-2,3-dicarbollide<sup>4</sup> and sodium cyclopentadienide was prepared from excess sodium hydride,  $(\text{CH}_3)_3\text{NHB}_9\text{C}_2\text{H}_{12}$ , and cyclopentadiene in tetrahydrofuran at the reflux temperature. The liberated  $(\text{CH}_3)_3\text{N}$  was swept from the reaction mixture with a stream of dry nitrogen. This solution was then added to a solution of 28.5 mmoles of ferrous chloride in tetrahydrofuran at the reflux temperature. After heating for an additional 15 min., the resulting red solution was cooled and filtered, and the solvent was evaporated to yield a red gum. The crude product mixture was extracted with a mixture of 75 ml. each of benzene and water and the solvents were separated. Addition of 150 ml. of pentane to the dried benzene extractant precipitated purple needles which were recrystallized from cyclohexane-benzene to yield pure VI, m.p. 181–182°, 1.25 g., 4.95 mmoles. *Anal.* Calcd. for  $(\text{B}_9\text{C}_2\text{H}_{11})\text{Fe}(\text{C}_5\text{H}_5)$ : Fe, 22.04; B, 38.42; C, 33.18; H, 6.36. Found: Fe, 21.63; B, 37.64; C, 30.59; H, 6.50. Evaporation of the benzene-pentane filtrate to dryness followed by recrystallization of the residue from methanol gave ferrocene, 1.55 g., 8.35 mmoles, identified by its infrared spectrum.

The aqueous layer from the extraction was treated with excess tetramethylammonium chloride and the precipitated salt washed with ethanol. The ethanol wash was evaporated to dryness and the residue recrystallized from acetone-water to give the tetramethylammonium salt of I, 0.95 g., 2.4 mmoles, identified by its characteristic infrared spectrum.

The reduction of VI to V was carried out at room temperature in acetone solution with dilute sodium amalgam. During the course of the reduction the

acetone solution changed from purple to orange. The excess amalgam was separated, the acetone solution evaporated to dryness, and the residue taken up in water. Addition of excess tetramethylammonium chloride precipitated the corresponding salt of V which was recrystallized from ethanol to yield orange plates (85%). *Anal.* Calcd. for  $(\text{CH}_3)_4\text{N}(\text{B}_9\text{C}_2\text{H}_{11})\text{Fe}(\text{C}_5\text{H}_5)$ : Fe, 17.05; B, 29.73; C, 40.33; N, 4.28; H, 8.61. Found: Fe, 17.86; B, 29.49; C, 37.47; N, 4.74; H, 8.55. In contrast to II, V was stable to oxidation by air. The  $^1\text{H}$  n.m.r. spectrum of tetramethylammonium V was consistent with its assigned structure as follows<sup>5</sup>: a broad carborane C-H resonance of intensity 2 at  $-3.58$  p.p.m.; a sharp singlet of intensity 12 at  $-3.09$  p.p.m. assigned to the methyl groups in the tetramethylammonium cation; and a sharp singlet of intensity 5 at  $-4.37$  p.p.m. assigned to cyclopentadienyl protons. In comparison, ferrocene exhibits a singlet at  $-4.17$  p.p.m.<sup>6</sup> The  $^{11}\text{B}$  n.m.r. spectrum of V closely resembles that of II and IV.

Paramagnetic VI and I gave the interesting  $^{11}\text{B}$  n.m.r. spectra shown in Figure 1. No  $^{11}\text{B}$ - $^1\text{H}$  coupling was observed<sup>7</sup> and these spectra extended over approximately 600 p.p.m. The wide separation of the individual  $^{11}\text{B}$  resonances is undoubtedly due to the presence of large contact shifts which involve the paramagnetic iron(III) atom. The great similarity of the two spectra presented in Figure 1 virtually proves that I bears two  $\pi$ -(1)-2,3-dicarbollyl<sup>4</sup> groups about iron as previously suggested.<sup>1</sup> The broad, highest-field resonances in I and VI (e) and the poorly defined (and probably quite broad) resonances in the b-c arrays must arise from the three boron atoms nearest iron(III) in I and VI.

The chemistry of the (1)-2,3- and (1)-2,4-dicarbollide ions<sup>4</sup> is under intensive investigation and further results will be reported at a later date.

*Acknowledgments.* The authors are indebted to Professor David Templeton and Dr. Allan Zalkin for the results of their structural studies received prior to publication. This research was generously supported by the Army Research Office (Durham).

(5) Relative to tetramethylsilane standard.

(6) G. Fraenkel, R. E. Carter, A. McLachlan and J. H. Richards, *J. Am. Chem. Soc.*, **82**, 5846 (1960).

(7) W. N. Lipscomb and A. Kaczmarczyk, *Proc. Natl. Acad. Sci. U. S. A.*, **47**, 1796 (1961), have observed the loss of  $^{11}\text{B}$ - $^1\text{H}$  coupling in  $^{11}\text{B}$  n.m.r. spectra obtained in the presence of  $\text{Fe}^{\text{III}}$ .

(8) Alfred P. Sloan Research Fellow.

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## The Crystal and Molecular Structure of $\text{C}_5\text{H}_5\text{FeB}_9\text{C}_2\text{H}_{11}$

Sir:

A compound designated  $\pi$ -cyclopentadienyl- $\pi$ -(1)-2,3-dicarbollyliron(III) was synthesized by Hawthorne and Pilling as described in the adjacent communication.<sup>1</sup> We determined its crystal structure by X-ray diffraction and found a "sandwich"-type molecular structure as predicted by Hawthorne. This work is the

(1) M. F. Hawthorne and R. L. Pilling, *J. Am. Chem. Soc.*, **87**, 3987 (1965).