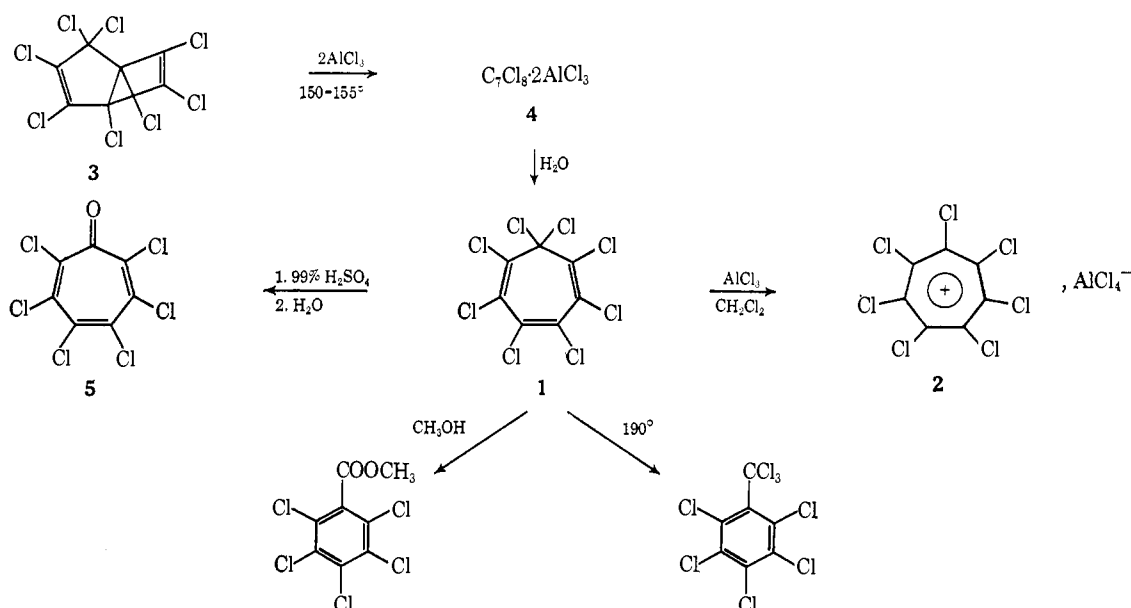


## Octachlorocycloheptatriene and Heptachlorotropenium Ion

Sir:

Several years ago the synthesis of tetrachlorocyclopropene<sup>1</sup> and its conversion into stable salts of the aromatic trichlorocyclopropenium ion<sup>2</sup> were reported. These compounds have become useful intermediates for the preparation of various three-membered ring compounds.<sup>3</sup> We now wish to report the isolation of the corresponding seven-membered ring species, octachlorocycloheptatriene (1) and heptachlorotropenium ion (2).

Treatment of the known compound octachlorobicyclo[3.2.0]hepta-2,6-diene (3)<sup>4</sup> with 2 equiv of aluminum chloride at 150–155° led to formation of a greenish complex (4) which yielded 1 upon quenching with water. The product was recrystallized from hexane to give pure 1 as colorless crystals, mp 86°.



*Anal.* Calcd for C<sub>7</sub>Cl<sub>8</sub>: C, 22.87; Cl, 77.13. Found: C, 22.94; Cl, 77.07. The formula C<sub>7</sub>Cl<sub>8</sub> for 1 is established by the elemental analysis and by the mass spectrum, which shows parent ion peaks clustering about *m/e* 366, 368 as well as a very strong peak for the C<sub>7</sub>Cl<sub>7</sub><sup>+</sup> ion (*m/e* 331, 333). Assignment of the octachlorocycloheptatriene structure for 1 follows from the nqr spectrum, which showed resonances at 37.0, 37.1, 37.4, 39.3, and 39.7 MHz with relative intensity 2:2:2:1:1. The lines at 37–37.4 MHz are in the proper region for vinylic chlorines,<sup>5</sup> whereas the lines at 39.3 and 39.7 MHz suggest two nonequivalent chlorine atoms in a CCl<sub>2</sub> group, as expected for a nonplanar molecule of 1. The chemical properties of 1, summarized in the reaction scheme, also support the

octachlorocycloheptatriene structure. In particular, 99% H<sub>2</sub>SO<sub>4</sub> converts 1 to the known compound hexachlorotropone (5) previously prepared by Scherer.<sup>6</sup> Compound 1, like 5, is easily transformed to derivatives of pentachlorobenzoic acid. Thus methanol converts 1 to methyl pentachlorobenzoate, mp 98–100° (lit.<sup>7</sup> 97°).<sup>8</sup> On simple heating to 185–190° 1 undergoes isomerization to octachlorotoluene, mp 68–70° (lit.<sup>9</sup> 71–72°).<sup>8</sup>

A most significant property of 1 is its reaction with metal halides which are strong Lewis acids to form salts of the heptachlorotropylium ion, C<sub>7</sub>Cl<sub>7</sub><sup>+</sup>. When 1 was treated with 1 equiv of aluminum chloride in dry dichloromethane, precipitation of the insoluble product began at room temperature. The mixture was heated to reflux for 1 hr to complete the reaction and then cooled, whereupon C<sub>7</sub>Cl<sub>7</sub><sup>+</sup>AlCl<sub>4</sub><sup>-</sup> was isolated by filtration in essentially quantitative yield, as a pale yellow powder. *Anal.* Calcd for C<sub>7</sub>AlCl<sub>11</sub>: C, 16.78; Cl,

77.83. Found: C, 16.79; Cl, 78.54. Similar 1:1 compounds are formed between 1 and antimony pentachloride or tin tetrachloride. Quenching of salts of 2 in water regenerates 1. The salts of 2 all show essentially identical infrared spectra above 600 cm<sup>-1</sup>, consisting of just four bands at 1252 (w), 1180 (s), 750 (w), and 700 cm<sup>-1</sup> (s). At lower frequencies bands characteristic of the chlorometallate anions are observed.

Although 2 is unlikely to be planar,<sup>10</sup> it seems to be at least as stable as the analogous three-membered ring cation C<sub>3</sub>Cl<sub>3</sub><sup>+</sup> (which does not form a pentachlorostannate). We believe that C<sub>7</sub>Cl<sub>7</sub><sup>+</sup> retains much of the aromatic character observed for tropenium ions generally.<sup>11</sup>

(1) S. W. Tobey and R. West, *Tetrahedron Letters*, 1179 (1963); *J. Am. Chem. Soc.*, **88**, 2481 (1966).

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(4) A. Roedig and L. Hörnig, *Ann. Chem.*, **598**, 208 (1956).

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(6) K. Scherer, Jr., *J. Am. Chem. Soc.*, **90**, 7352 (1968).

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(11) W. von E. Doering in "Theoretical Organic Chemistry (Kekule Symposium)," Butterworth and Co. (Publishers), Ltd., London, 1958, pp 35–48.

The structure of **2** and the reactions of **1** and **2** are under investigation.

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### The Formation of $CB_5H_9$ and Its 1-Methyl Derivative from 1,7- $C_2B_6H_8$

Sir:

We wish to report the preparation of the parent member of the  $CB_nH_{n+4}$  carborane series, where  $n = 5$ , 2-carbahexaborane(9),  $CB_5H_9$ ,<sup>1</sup> and its 1-methyl derivative, both of which have not been previously reported, although several alkyl derivatives are known.<sup>1-3</sup>

The reaction between 1,7-dicarba-*closo*-octaborane(8),  $C_2B_6H_8$ ,<sup>4-6</sup> and tetramethylammonium borohydride<sup>7</sup> in diglyme at 100° for 24 hr yields as yet uncharacterized ionic products. Removal of the solvent by vacuum distillation followed by heating at 85° *in vacuo* for 10 hr produced a solvent-free solid. The solid was then treated with an excess of dry HCl, and a mixture of neutral compounds was liberated and separated using standard vpc methods. Three major fractions were collected and characterized.

The mass spectrum of 2-carbahexaborane(9),  $CB_5H_9$  (Figure 1), the major fraction formed in approximately 20% yield, exhibited a cutoff at  $m/e$  76 which corresponds to the  $^{12}C^{11}B_5^+H_9^+$  ion. The 60-Mc/sec  $^1H$  nmr spectrum consisted of a broad peak at  $\tau$  4.62 relative to internal tetramethylsilane (TMS). The  $^{11}B$  nmr spectrum (Figure 1) consisted of three sets of doublets of relative area 2:2:1 which is consistent with a species containing five borons in a pentagonal pyramid structure. The doublet at lowest field shows secondary splitting due to bridge hydrogen coupling.

The mass spectrum of 1-methyl-2-carbahexaborane(9), 1- $CH_3CB_5H_8$ , exhibited a cutoff at  $m/e$  90 which corresponds to the  $^{12}C_2^{11}B_3^+H_{11}^+$  ion. The 60-Mc/sec  $^1H$  nmr spectrum consisted of a broad peak of relative area 3 at  $\tau$  10.58 and a broad peak of relative area 1 at  $\tau$  4.45 relative to internal TMS. The  $^{11}B$  nmr spectrum (Figure 1) consisted of two sets of doublets and a singlet of relative area 2:2:1, respectively. The high-field singlet indicates substitution at the 1 position.

The third fraction identified from the reaction was 3-methyl-2-carbahexaborane(9), 3- $CH_3CB_5H_8$ , which was identical with that reported earlier.<sup>1</sup>

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(7) Sodium borohydride gives similar results; however, the ionic species formed is difficult to separate from residual solvent.

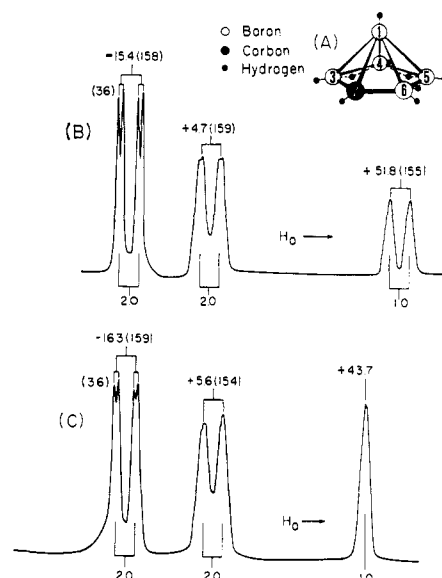


Figure 1. (A) The molecular structure of 2-carbahexaborane(9),  $CB_5H_9$ . The 32.1-Mc/sec  $^{11}B$  nmr spectra of  $CB_5H_9$  (B) and 1- $CH_3CB_5H_8$  (C). Chemical shifts (ppm, relative to  $BF_3 \cdot O(C_2H_5)_2$ ) and coupling constants (cps) are indicated. Relative areas appear beneath the peaks.

Even though the removal of boron atoms from carborane cages is well known both by pyrolytic and chemical methods,<sup>6,8-13</sup> this appears to be the first example of the removal of cage carbon atoms from a closed carborane.

The characterization of the ionic species and several minor components also obtained in this reaction, together with the results of the reaction between C-methyl and C,C'-dimethyl-1,7-dicarba-*closo*-octaborane(8) with borohydride ion, will be presented elsewhere.

**Acknowledgment.** This research was supported in part by the Office of Naval Research.

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### The Nuclear Overhauser Enhancement of the Carbon-13 Magnetic Resonance Spectrum of Formic Acid

Sir:

The difficulties associated with detecting the carbon-13 isotope in its 1.1% natural abundance are well known, and therefore it is important to characterize the dramatic improvement in the ratio of signal to noise realized with proton decoupling methods. In addition to the enhancement expected from proton multiplet collapse, application of a proton decoupling radio-