Sir:

7354

Several years ago the synthesis of tetrachlorocyclopropene¹ and its conversion into stable salts of the aromatic trichlorocyclopropenium ion² were reported. These compounds have become useful intermediates for the preparation of various three-membered ring compounds.³ 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 $(3)^4$ 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°.

octachlorocycloheptatriene structure. In particular, 99% H₂SO₄ converts 1 to the known compound hexachlorotropone (5) previously prepared by Scherer.⁶ Compound 1, like 5, is easily transformed to derivatives of pentachlorobenzoic acid. Thus methanol converts 1 to methyl pentachlorobenzoate, mp 98-100° (lit.⁷ 97°).⁸ On simple heating to 185–190° 1 undergoes isomerization to octachlorotoluene, mp 68-70° (lit.⁹ 71-72°).8

A most significant property of 1 is its reaction with metal halides which are strong Lewis acids to form salts of the heptachlorotropylium ion, $C_7Cl_7^+$. 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 $C_7Cl_7^+AlCl_4^-$ was isolated by filtration in essentially quantitative yield, as a pale yellow powder. Anal. Calcd for C7AlCl11: C, 16.78; Cl,



Anal. Calcd for C₇Cl₈: C, 22.87; Cl, 77.13. Found: C, 22.94; Cl, 77.07. The formula C_7Cl_8 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 $C_7Cl_7^+$ ion (*m/e* 331, 333). Assignment of the octachlorocycloheptatriene structure for 1 follows from the ngr 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,⁵ whereas the lines at 39.3 and 39.7 MHz suggest two nonequivalent chlorine atoms in a CCl₂ group, as expected for a nonplanar molecule of 1. The chemical properties of 1, summarized in the reaction scheme, also support the

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

(2) S. W. Tobey and R. West, *ibid.*, **86**, 1459 (1964); R. West, A. Sado, and S. W. Tobey, *ibid.*, **88**, 2488 (1966).

(3) For examples see S. W. Tobey and R. West, *ibid.*, **86**, 4215 (1964); R. West and D. C. Zecher, *ibid.*, **89**, 153 (1967); R. Breslow and G. Ryan, ibid., 89, 3073 (1967); R. Breslow, J. T. Groves, and G. Ryan, ibid., 89, 5048 (1967).

(4) A. Roedig and L. Hörnig, Ann. Chem., 598, 208 (1956).
(5) Structural correlations for chlorine ngr frequencies in polychlorinated organic compounds will be published at a later date.

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⁻¹, consisting of just four bands at 1252 (w), 1180 (s), 750 (w), and 700 cm^{-1} (s). At lower frequencies bands characteristic of the chlorometallate anions are observed.

Although 2 is unlikely to be planar, ¹⁰ it seems to be at least as stable as the analogous three-membered ring cation $C_3Cl_3^+$ (which does not form a pentachlorostannate). We believe that $C_7Cl_7^+$ retains much of the aromatic character observed for tropenium ions generally.¹¹

(8) The identification of this compound is further supported by its ngr spectrum, which will be published separately.

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(10) Attempts to observe an nqr spectrum for salts of 1 have so far been unsuccessful. Whether this is due to disorder of the cation in the structures, to poor crystallinity, or to other causes is not yet clear. (11) W. von E. Doering in "Theoretical Organic Chemistry (Kekule

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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 CB₅H₉ and Its 1-Methyl Derivative from $1.7 - C_2 B_6 H_8$

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), CB₅H₉,¹ and its 1-methyl derivative, both of which have not been previously reported, although several alkyl derivatives are known. 1-3

The reaction between 1,7-dicarba-closo-octaborane-(8), $C_2B_6H_{8}$, ⁴⁻⁶ and tetramethylammonium borohydride⁷ 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 ${}^{12}C^{11}B_5{}^{1}H_9^+$ ion. The 60-Mc/sec ${}^{1}H$ nmr spectrum consisted of a broad peak at τ 4.62 relative to internal tetramethylsilane (TMS). The ¹¹B 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.

mass spectrum of 1-methyl-2-carbahexa-The borane(9), 1-CH₃CB₅H₈, exhibited a cutoff at m/e 90 which corresponds to the ${}^{12}C_2{}^{11}B_5{}^{1}H_{11}{}^+$ ion. The 60-Mc/sec ¹H nmr spectrum consisted of a broad peak of relative area 3 at τ 10.58 and a broad peak of relative area 1 at τ 4.45 relative to internal TMS. The ¹¹B 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 3methyl-2-carbahexaborane(9), 3-CH₃CB₅H₈, which was identical with that reported earlier.¹

(1) T. P. Onak, G. B. Dunks, J. R. Spielman, F. J. Gerhart, and R. E. (1) 1.1.1. of Char, O. D. Danks, O. A. Spinstein, T. S. Cethar, Williams, J. Am. Chem. Soc., 88, 2061 (1966).
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(6) G. B. Dunks and M. F. Hawthorne, Inorg. Chem., 7, 1038 (1968). (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 ¹¹B 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, 6,8-13 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 Cmethyl 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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(13) J. N. Francis and M. F. Hawthorne, ibid., 90, 1663 (1968).

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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-