

length together with the moments of inertia from the microwave study<sup>8</sup> to derive a value for the CPH angle. The value obtained is dependent on several assumptions but it lies between 97.3 and 99.6° for all reasonable assumptions. From the present study the CPF angle is found to be 97.8°. Thus, although the CPF angle in CH<sub>3</sub>PF<sub>2</sub> may be smaller than the CPH angle in CH<sub>3</sub>PH<sub>2</sub>, the difference is definitely less than the 7.4° difference found in the amines.

The dipole moment of CH<sub>3</sub>PF<sub>2</sub> is 2.06 D; this is 0.74 D greater than the dipole moment of HPF<sub>2</sub>.<sup>7</sup> A similar effect is found when we compare the dipole moments of CH<sub>3</sub>NF<sub>2</sub><sup>10</sup> (2.57 D) and HNF<sub>2</sub><sup>13</sup> (1.92 D).

After making several assumptions we have obtained a

(13) D. R. Lide, *J. Chem. Phys.*, **38**, 456 (1963).

value for the PC bond length of 1.82 Å; this compares with a value of 1.858 Å in CH<sub>3</sub>PH<sub>2</sub>.<sup>12</sup> This shortening effect observed on introducing fluorine atoms is well known: the pH bond length in HPF<sub>2</sub> is 1.412 Å<sup>7</sup> compared to 1.421 Å in PH<sub>3</sub>;<sup>14</sup> the CN bond length in CH<sub>3</sub>NF<sub>2</sub> is 1.449 Å<sup>10</sup> compared to 1.474 Å in CH<sub>3</sub>NH<sub>2</sub>.<sup>9</sup>

Hence, with respect to structure, dipole moment, and barrier to internal rotation CH<sub>3</sub>PF<sub>2</sub> behaves in just the manner expected from a consideration of related molecules.

**Acknowledgment.** We acknowledge with appreciation the gift of a sample of CH<sub>3</sub>PF<sub>2</sub> from Dr. K. Cohn.

**Registry No.** CH<sub>3</sub>PF<sub>2</sub>, 753-59-3.

(14) C. A. Burrus, A. Jache, and W. Gordy, *Phys. Rev.*, **95**, 706 (1954).

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## Synthesis and Properties of 1,2-(2,3-Naphtho)-*o*-carborane<sup>1</sup>

DONALD S. MATTESON\* and ROGER A. DAVIS

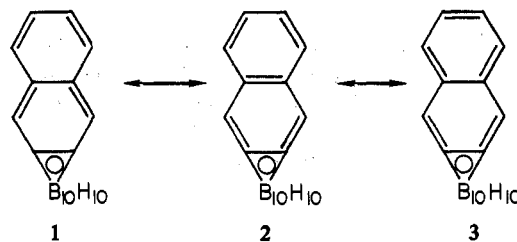
Received August 16, 1973

Naphthocarborane has been synthesized, starting from dilithio-*o*-carborane and  $\alpha,\alpha'$ -dibromo-*o*-xylene, to form dihydronaphthocarborane, which on allylic bromination with *N*-bromosuccinimide yielded dibromodihydronaphthocarborane instead of the expected monobromo compound. Debromination with sodium iodide gave naphthocarborane, an air-sensitive, fluorescent yellow solid. Naphthocarborane readily adds bromine to the inner ring to form dibromodihydronaphthocarborane, oxygen to the inner ring to form a polymeric peroxide, and maleic anhydride or dimethyl acetylenedicarboxylate to the outer ring to form the corresponding Diels-Alder adduct. The proton nmr absorption of the outer ring of naphthocarborane appears at the same position as that of the ring protons of *p*-xylylene, which indicates that there is little if any effective  $\pi$  bonding between the cage and the ring system.

### Introduction

Naphthocarborane<sup>2</sup> (1) (Figure 1) was chosen for study in the hope of answering some questions about the possible aromaticity of rings fused to carborane cages, which have only been partially answered by our studies of benzocarborane<sup>3</sup> and benzodicarbollide ion derivatives.<sup>4</sup> In the isomer chosen, the outer benzenoid ring can be fully aromatic only if the inner ring is also aromatic, with strong conjugation between the orbitals of the icosahedral cage and the  $\pi$  orbitals of the ring. Expressed in the terminology of resonance, structure 1 must be a polyene unless 2 and 3 contribute significantly to the resonance hybrid.

The outer ring of naphthocarborane is far enough from the carborane cage so that some of the ambiguities in distin-



guishing electron delocalization effects from the steric and inductive effects of the cage encountered in the case of benzocarborane<sup>3</sup> might be resolved. It was also hoped that the extra delocalization energy to be gained by making a second ring aromatic might cause an increase in the ring-cage conjugation. However, it has turned out that naphthocarborane has some new ambiguities of its own, and the hope of proving that ring-cage conjugation is a significant structural feature has not been fulfilled.

### Results

**Synthesis.** We expected that our synthesis of benzocarborane<sup>3</sup> would be readily adaptable to the preparation of naphthocarborane (1). It was, but not without some unexpected twists. The reaction of dilithio-*o*-carborane with  $\alpha,\alpha'$ -dibromo-*o*-xylene efficiently yielded 5,8-dihydronaphthocarborane (4).<sup>5</sup> However, bromination of 4 with *N*-bromosuccinimide did not yield the expected 5-bromo-5,8-

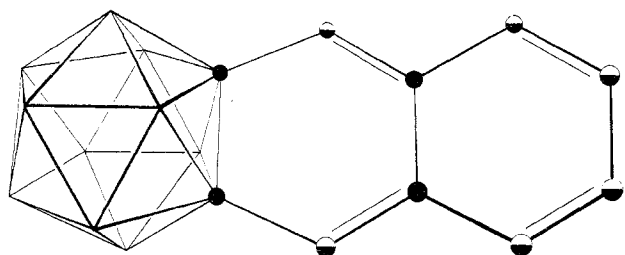
(1) (a) Preliminary communication by D. S. Matteson and R. A. Davis, *J. Chem. Soc. D*, 669 (1970); (b) supported by U. S. Public Health Service Research Grant No. CA-05513 from the National Cancer Institute; (c) abstracted from the Ph.D. Thesis of R. A. D., Washington State, University, 1971.

(2) A possible systematic name would be 1,2-(2,3-naphtho)-1,2-dicarba-*closo*-dodecaborane(12). By the system commonly in use for naming polycyclic compounds, possible names are naphtho-[2,3-*a*]-1,2-dicarba-*closo*-dodecaborane(12) or, in a system which would avoid any ambiguity in lettering higher numbered edges of the icosahedron, 1,2-dicarba-*closo*-dodecaborano(12)[1,2-*b*] naphthalene. There is, of course, another possible isomer, 1,2-(1,2-naphtho)-1,2-dicarba-*closo*-dodecaborane(12), but it would shed no light on the question of aromaticity raised here since it would have an aromatic benzene ring regardless of ring-cage interaction.

(3) (a) N. K. Hota and D. S. Matteson, *J. Amer. Chem. Soc.*, **90**, 3570 (1968); (b) D. S. Matteson and N. K. Hota, *ibid.*, **93**, 2893 (1971).

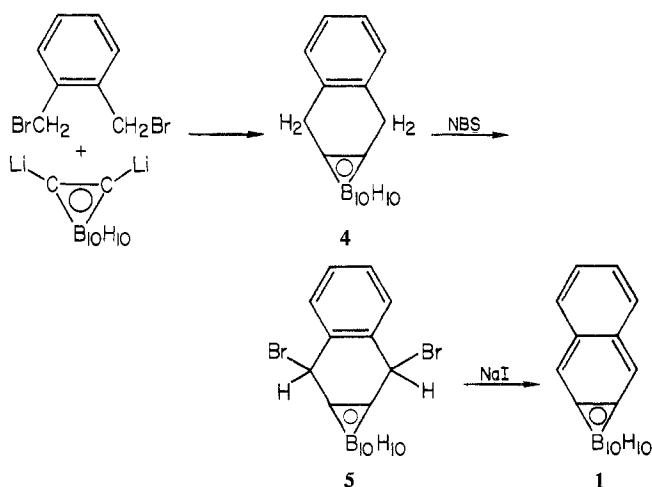
(4) D. S. Matteson and R. E. Grunzinger, Jr., *Inorg. Chem.*, **13**, 671 (1974).

(5) We have arbitrarily numbered the rings of naphthocarborane like naphthalene, starting with 1, 2, 3, 4 for the CH groups of the outer ring and 5, 8 for those of the inner ring.

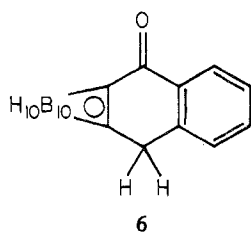


**Figure 1.** Structure diagram of 1,2-(2,3-naphtho)-*o*-carborane (1). Black circles represent C, half-filled circles CH, and unmarked line junctions BH.

dihydronaphthocarborane but instead gave 5,8-dibromo-5,8-dihydronaphthocarborane (5). We have not established whether 5 is the *cis* or the *trans* isomer. The successful combination for debromination of 5 to naphthocarborane turned out to be sodium iodide in acetone, with strict exclusion of atmospheric oxygen.



Before finding the successful combination, we tried to debrominate 5 with zinc dust in dimethylformamide. A yellow solution was obtained, but on aqueous work-up the only products isolated were dihydronaphthocarborane (4) and 5-keto-5,8-dihydronaphthocarborane (6).



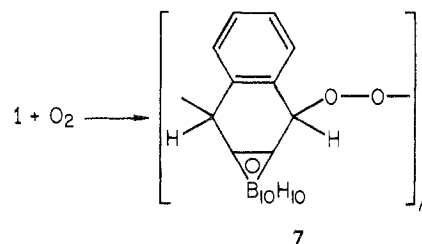
Attempts to dehydrogenate dihydronaphthocarborane (4) with palladium on charcoal or rhodium on alumina in refluxing xylene failed. After 48 hr only unconverted 4 was recovered.

Attempted dehydrohalogenation of the dibromo compound (5) with pyridine gave material which yielded a low boron analysis (~25%) and was clearly not bromonaphthocarborane. This was not pursued further.

**Physical Properties.** Naphthocarborane is a fluorescent yellow solid. The electronic absorption spectrum shows a series of bands to as long as  $\lambda_{\text{max}}$  414 nm ( $\epsilon$  2400), and the fluorescence  $\lambda_{\text{max}}$  is 447 nm (in 2,2,4-trimethylpentane). The nmr spectrum shows only two CH peaks, the 1,2,3,4-hydrogens appearing at  $\delta$  6.50 and the 5,8-hydrogens at

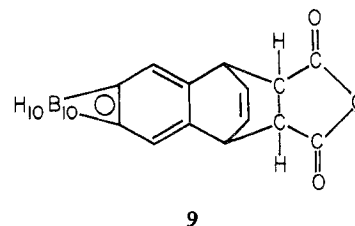
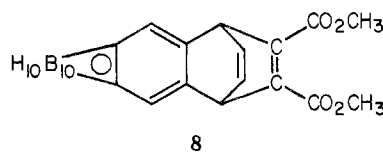
$\delta$  6.65 (relative to internal tetramethylsilane in carbon tetrachloride).

**Reactions.** In contrast to benzocarborane,<sup>3</sup> naphthocarborane (1) is highly reactive toward a variety of electrophilic reagents. The first one we had to contend with was atmospheric oxygen, which attacks solutions of 1 fairly rapidly, the solid more slowly, to yield a polymeric peroxide (7). A sample we obtained had a molecular weight of 1700 and showed a broadened CH band in the nmr at  $\delta$  7.35. This nmr spectrum indicates that the oxygen adds to the 5,8-positions (inner ring), allowing the outer ring to become fully aromatic.



Bromine readily adds to naphthocarborane (1) to regenerate 5,8-dibromo-5,8-dihydronaphthocarborane (5). Although naphthocarborane can be purified by rapid recrystallization from methanol-water, a more leisurely recrystallization from these solvents led instead to 5-ketodihydronaphthocarborane (6), which has already been mentioned as a by-product of the zinc reduction of 5. Although 6 was not obtained analytically pure, its mass spectrum, the nmr peaks at  $\delta$  3.57 (CH<sub>2</sub>) and 7.39 (aromatic CH), and the carbonyl band in the ir at 1720 cm<sup>-1</sup> are sufficient to confirm the structure. Air oxidation of 1 could be the source of 6.

Some dienophiles also add readily to naphthocarborane (1). In contrast to reagents which can attack one site at a time, they are sterically forced to add to the outer ring (1,4-positions). The structures of the adducts are established by their nmr spectra, which show no absorptions downfield from  $\delta$  6.6–6.85, too high for fully aromatic protons ( $\delta$  7.17–7.4) which would arise if addition were to the inner ring, leaving the outer aromatic.<sup>6</sup> Dimethyl acetylenedicarboxylate gave the adduct 8 and maleic anhydride gave 9.



One might expect naphthocarborane (1) to react very rapidly with tetracyanoethylene (TCNE). Surprisingly, we were unable to make the reaction go at all and recovered unchanged 1 after 8 hr in a sealed tube at 110° or refluxing

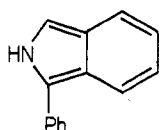
(6) The peaks assigned to the bridgehead protons,  $\delta$  4.62 in 8 and 4.07 in 9, might seem too far downfield for saturated CH but are consistent with other bridgehead CH observed in bicyclooctenes: H. E. Zimmerman, G. L. Grunewald, R. M. Paufler, and M. A. Sherwin, *J. Amer. Chem. Soc.*, 91, 2330 (1969).

in tetrahydrofuran. The tetrahydrofuran solution immediately turned blue-green, suggesting possible  $\pi$  complex formation between **1** and TCNE.

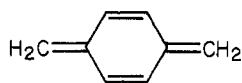
### Discussion

The aromatic character of both benzenoid rings of naphthocarborane (**1**) is clearly impaired by poor conjugation at the ring-cage junction. All that is left to discuss is whether the available evidence supports or refutes the presence of a small degree of ring-cage conjugation.

The reactivity of naphthocarborane is reminiscent of heterocyclic compounds containing a similar set of double bonds. For example, 1-phenylisoindole (**10**) has been reported to be a yellow ( $\lambda_{\max} \sim 355$  nm) compound which resinifies in air.<sup>7</sup> It reacts readily with maleic anhydride but yields a substitution product involving the heterocyclic ring, in contrast to the addition product at the outer ring obtained with naphthocarborane. The nmr spectra of the isoindoles were not reported in detail, but one of them was said to show aromatic (including phenyl) absorptions at  $\delta$  6.8–8.05, which is all downfield from the 1,2,3,4-hydrogens (outer ring) of naphthocarborane ( $\delta$  6.50). Isoindoles clearly do have a considerable degree of aromatic character, enough to favor them over tautomeric indolenines in which the cyclic conjugation is broken.<sup>7</sup> It appears that naphthocarborane has less aromatic character than 1-phenylisoindole (**10**).



10



11

*p*-Xylylene (**11**) is another useful reference compound. The ring protons of **11** appear at  $\delta$  6.49 in the nmr,<sup>8</sup> the same within experimental error as the 1,2,3,4-protons of naphthocarborane. The terminal protons of **11** appear considerably upfield at  $\delta$  5.10. The corresponding 5,8-protons of naphthocarborane appear at  $\delta$  6.65 and are therefore shifted downfield by some combination of aromatic character in the ring and the inductive effect of the carborane cage. *p*-Xylylene reacts very rapidly with oxygen to form a peroxide<sup>9</sup> analogous to that (**7**) formed more slowly from naphthocarborane. In contrast to naphthocarborane, *p*-xylylene dimerizes and is not isolable. *o*-Xylylene might be a better reference compound, but it is more reactive and more difficult to study than the para isomer. Very recently, the fluorescence  $\lambda_{\max}$  has been reported to be 456 nm, the absorption  $\lambda_{\max}$  373 nm, and  $\epsilon_{\max} > 3000$ , but nmr data could not be obtained.<sup>10</sup>

None of the foregoing provides any evidence of any ring-cage conjugation in naphthocarborane at all. The outer ring of naphthocarborane clearly has some aromatic character, but it could be argued from the nmr spectra that the ring of *p*-xylylene has just as much, which is of course the minimum possible for a six-membered ring of this type, where no benzenoid resonance structures can be written but molecular orbital calculations predict some aromaticity. The relative

stability of naphthocarborane compared to *o*- or *p*-xylylene may be attributed to severe steric hindrance. In fact, the reactivity of the outer ring of naphthocarborane probably provides a good first approximation to what the reactivity of the ring in *o*-xylylene would be like if it were not completely overshadowed by that of the terminal carbons.

Two anomalies in the observed chemistry require comment. The formation of 5,8-dibromo-5,8-dihydronaphthocarborane (**5**) from 5,8-dihydronaphthocarborane (**4**) even with a deficiency of *N*-bromosuccinimide is strange. Perhaps the monobromo compound undergoes dehydrobromination under the reaction conditions (as does the analogous benzo-carborane precursor to some extent<sup>3</sup>), and the resulting naphthocarborane would then be expected to add bromine, as observed in a separate experiment.

The other anomaly is the failure of naphthocarborane (**1**) to react with tetracyanoethylene (TCNE). This result implies that the carborane cage of **1** somehow hinders normal Diels-Alder addition of TCNE even at the outer ring. Although it is not obvious from the drawing (Figure 1), the cage hydrogens do project a considerable distance in front and in back of the inner rings, and inspection of models suggests that attack of TCNE on **1** could perhaps be hindered even at the outer ring. However, this requires that **1** be extremely rigid, and it suggests that the rings may be pulled closer in toward the cage than pictured in Figure 1, perhaps by a widening of the bond angles at the ring-cage junction.

We conclude that the properties of naphthocarborane (**1**) can be accounted for to a good first approximation by assuming there is no ring-cage  $\pi$  bonding at all. However, the evidence does not require that such interaction be nonexistent, and is not in conflict with other studies in which it appeared that there is a small degree of ring-cage  $\pi$  bonding in benzocarborane<sup>3</sup> and benzodicarbollide derivatives.<sup>4</sup>

### Experimental Section

**5,8-Dihydronaphthocarborane (4).** A solution of 5.85 g (0.04 mol) of *o*-carborane in 50 ml of ether was added in 15 min with stirring to 50 ml (0.08 mol) of 1.6 *M* butyllithium in hexane at  $-10^\circ$ . The mixture was stirred 1 hr at  $25^\circ$  and refluxed 15 min. A solution of 12.5 g (0.047 mol) of  $\alpha, \alpha'$ -dibromo-*o*-xylene in 100 ml of ether was added with stirring over a period of 45 min. The mixture was refluxed 5 hr and then treated with 50 ml of water. The organic phase was concentrated under vacuum and the residue was sublimed at  $120^\circ$  (0.1 mm) and then recrystallized from methylcyclohexane: yield of **4**, 8.6 g (87%); mp  $186$ – $187^\circ$ ; nmr ( $\text{CCl}_4$ )  $\delta$  3.75 (s, 4,  $\text{CH}_2$ ), 7.17 (m, 4,  $\text{C}_6\text{H}_4$ ); mass spectrum  $m/e$  246 ( $\text{C}_{10}\text{H}_{18}^{10}\text{B}_2^{11}\text{B}_8^+$ ) with isotopic satellites. *Anal.* Calcd for  $\text{C}_{10}\text{H}_{16}\text{B}_{10}$ : C, 48.76; H, 7.37; B, 43.88. Found: C, 48.89; H, 7.45; B, 44.12.

**5,8-Dibromo-5,8-dihydronaphthocarborane (5).** A solution of 6.65 g (0.027 mol) of dihydronaphthocarborane (**4**) in 125 ml of carbon tetrachloride was refluxed 12 hr under nitrogen with 9.6 g (0.054 mol) of *N*-bromosuccinimide and a few mg of benzoyl peroxide. The mixture was filtered and the filtrate was concentrated under vacuum. The residue was chromatographed on silica gel with cyclohexane as the eluent. After recrystallization from methylcyclohexane the yield of **5** was 5.4 g (48%); mp  $196$ – $197^\circ$ ; nmr ( $\text{CDCl}_3$ )  $\delta$  5.82 (s, 2,  $\text{CHBr}$ ), 7.30 (s, 4,  $\text{C}_6\text{H}_4$ ). *Anal.* Calcd for  $\text{C}_{10}\text{H}_{16}\text{B}_{10}\text{Br}_2$ : C, 29.72; H, 3.99; B, 26.75; Br, 39.54. Found: C, 30.00; H, 4.01; B, 26.59; Br, 39.43.

**Naphthocarborane (1).** The solvents used in this preparation were all pretreated by bubbling a slow stream of argon through them for 2 hr to remove dissolved oxygen, and all operations were carried out under an argon atmosphere. A solution of 3.50 g (8.65 mmol) of the dibromo compound **5** in 50 ml of anhydrous acetone was treated with 20 g of sodium iodide and the mixture was stirred and refluxed 1 hr. Water (100 ml) was added, which precipitated a yellow solid. The solid was filtered and was sublimed at  $180^\circ$  (0.1 mm) to yield 1.22 g (58%) of **1**. The analytical sample was recrystallized rapidly from methanol-water (prolonged exposure causes degradation to **6**); mp  $152$ – $159^\circ$  (sealed capillary); mass spectrum

(7) D. F. Veber and W. Lwowski, *J. Amer. Chem. Soc.*, **86**, 4152 (1964).

(8) D. J. Williams, J. M. Pearson, and M. Levy, *J. Amer. Chem. Soc.*, **92**, 1436 (1970).

(9) L. A. Errede and S. L. Hopwood, Jr., *J. Amer. Chem. Soc.*, **79**, 6507 (1957).

(10) C. R. Flynn and J. Michl, *J. Amer. Chem. Soc.*, **95**, 5802 (1973).

*m/e* 244 ( $C_{10}H_{16}^{10}B_2^{11}B_8^+$ ) with isotopic satellites; uv-vis (2,2,4-trimethylpentane)  $\lambda_{max}$  414 ( $\epsilon$  2400), 393 (3140), 377 (2420), 355 (1360), 335 (400), 280 nm (35,000); nmr ( $CCl_4$ )  $\delta$  6.50 (s, 4,  $C_6H_4$ ), 6.65 (s, 2, inner ring *CH*). *Anal.* Calcd for  $C_{10}H_{16}B_{10}$ : C, 49.16; H, 6.60; B, 44.24. Found: C, 49.13; H, 6.62; B, 44.32.

**Bromination of Naphthocarborane (1).** A 200-mg sample of naphthocarborane (1) in a few milliliters of carbon tetrachloride was treated with bromine until the bromine color persisted. Concentration and sublimation yielded 300 mg (90%) of dibromodihydronaphthocarborane (5), confirmed by mixture melting point and nmr.

**Naphthocarborane Peroxide Polymer (7).** Stirring a 2% solution of naphthocarborane 8 hr under air yielded a white precipitate which would not sublime; mol wt (osmometric in  $CHCl_3$ ) 1700; nmr ( $CDCl_3$ )  $\delta$  7.35 (broad s, 4,  $C_6H_4$ ), 5.5 (broad s, 2, O-*CH*); mass spectrum *m/e* 276, suggesting the presence of or breakdown to  $C_{10}H_{16}B_{10}O_2$ . *Anal.* Calcd for  $(C_{10}H_{16}B_{10}O_2)_n$ : C, 43.5; H, 5.8; B, 39.1. Found: C, 44.06; H, 6.21; B, 35.16.

**Adduct 8 of Naphthocarborane with Dimethyl Acetylenedicarboxylate.** A Pyrex glass tube was purged with argon, and in it were sealed 244 mg (1 mmol) of naphthocarborane (1) and 124 mg (1 mmol) of freshly redistilled dimethyl acetylenedicarboxylate. The mixture was heated at 100° for 8 hr and the tube was then cooled to 25° and opened. Recrystallization from methanol-water yielded 350 mg (91%) of 8; mp 214–215°; nmr ( $CDCl_3$ )  $\delta$  3.76 (s, 6,  $OCH_3$ ), 4.62 (m, 2, bridgehead *CH*); 6.28 (s, 2, inner ring *CH*); 6.59 (m, 2, *HC=CH*); ir (KBr)  $C=O$  at 1660  $cm^{-1}$ . *Anal.* Calcd for  $C_{16}H_{22}B_{10}O_4$ : C, 49.73; H, 5.74; B, 27.98. Found: C, 49.62; H, 5.72; B, 29.97.

**Adduct 9 of Naphthocarborane with Maleic Anhydride.** By the same procedure described for the preparation of 8, substituting maleic anhydride in place of dimethyl acetylenedicarboxylate, and

recrystallizing the product (9) from acetone-petroleum ether, an 88% yield was obtained; nmr ( $DMSO-d_6$ ):  $\delta$  3.43 (m, 2, *HCC=O*), 4.07 (m, 2, bridgehead *CH*), 6.48 (m, 2, *HC=CH*), 6.85 (s, 2, inner ring *CH*); ir (KBr) 1770  $cm^{-1}$  ( $C=O$ ). The compound was not analyzed.

**Attempted Reactions of Naphthocarborane with Tetracyanoethylene (TCNE).** The sealed tube method described for the preparation of 8 and 9 was attempted with TCNE, but the nmr spectrum of the resulting material was that of unconverted naphthocarborane. A mixture of 150 mg of naphthocarborane and 84 mg of tetracyanoethylene in 50 ml of anhydrous tetrahydrofuran immediately turned blue-green, but after 8 hr of reflux under argon only TCNE and naphthocarborane were recovered.

**5-Ketodihydronaphthocarborane (6).** This compound was isolated from an attempt to debrominate the dibromo compound (5) with zinc. A solution of 1.5 g of 5 in 50 ml of freshly distilled dimethylformamide was stirred under nitrogen for 8 hr. The solution immediately turned yellow. The dimethylformamide was distilled under vacuum and the residue was recrystallized from methanol-water, yielding 6; mp 138–149°; mass spectrum *m/e* 260 ( $C_{10}H_{16}^{10}B_2^{11}B_8O^+$ ); nmr ( $CDCl_3$ )  $\delta$  3.57 (s, 2, *CH\_2*), 7.39 (m, 4,  $C_6H_4$ ), and impurities at 4.62 and 5.89; ir (KBr) 1720  $cm^{-1}$  ( $C=O$ ). *Anal.* Calcd for  $C_{10}H_{16}B_{10}O$ : C, 46.13; H, 6.19; B, 41.53. Found: C, 48.64; H, 7.36; B, 41.01.

**Registry No.** 4, 23810-12-0; 5, 27120-76-9; 1, 27120-74-7; 7, PM50276-14-7; 8, 27120-77-0; 9, 50276-19-2; 6, 50276-20-5; dilitio-*o*-carborane, 22220-85-5;  $\alpha,\alpha'$ -dibromo-*o*-xylene, 91-13-4; dimethyl acetylenedicarboxylate, 762-42-5; maleic anhydride, 108-31-6.

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## Ionic Organoboranes. V. Preparations of Dicarbahemiosenium<sup>1,2</sup> and Dicarbaousenium Cations and a Neutral Ousene<sup>3,4</sup>

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Received March 20, 1973

Tropenyl methyl ether reacts with mono- or dilitio salts of *o*- or *m*-carborane to give tropenyl (7-cyclohepta-1,3,5-trienyl) carboranes. Rearrangement to  $\gamma$ -tropenyl (3-cyclohepta-1,3,5-trienyl) carboranes followed by hydride abstraction yields mono- or ditropenylumylcarboranes (dicarbahemiosenium and dicarbaousenium ions). Electronic, infrared, and <sup>1</sup>H and <sup>11</sup>B nmr spectra and nucleophile-exchange studies by nmr demonstrate destabilization of the ring by the *-I* cage and little  $\pi$  interaction between cage and ring. Unlike most tropenylum ions, these cations form covalent bromides. The syntheses of a neutral [7.7.10<sup>2,x</sup>]ousene and several tropenylumyl derivatives of the  $C_2B_9H_{11}(CH_3)^-$  anion are also reported.

### Introduction

As part of a program directed toward the synthesis of ionic polymers based on repeating patterns of carbocyclic cationic rings, polyhedral borane anion cages, and neutral carboranes (Figure 1) we have previously reported on the preparation

(1) The ousene nomenclature has been discussed in detail.<sup>2</sup> In brief, the parent name *ousene* is assigned to a  $B_nH_n^{2-}$  closo anion substituted with two aromatic carbocyclic cation rings; the numbers of carbons in the rings and borons in the cage are given in brackets before the name, with the boron number last, and superscript numbers on the boron number designate the position of the rings on the cage. The prefix *hemi* is used for a compound with a single ring on the cage, and the endings *ium* and *ide* are used to indicate cations and anions, respectively. The presence of carbons in the cage is represented by *carba* or *dicarba* in the conventional manner for carboranes. Examples of this nomenclature applied to compounds discussed in the paper are shown in Figure 2.

(2) K. M. Harmon, A. B. Harmon, and A. A. MacDonald, *J. Amer. Chem. Soc.*, **91**, 323 (1969).

(3) Work supported by the National Science Foundation and by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

and properties of the [7.10<sup>2</sup>]- and [7.12]hemiosenide ions<sup>2,6,7</sup> in which a tropenylumyl<sup>8,9</sup> group is linked to a borane anion cage and report herein on the characterization of a neutral [7.7.10<sup>2,x</sup>]ousene<sup>10</sup> in which the cage is flanked by two cationic rings (Figure 2). These highly colored, zwitterionic compounds show internal charge-transfer absorptions and extensive electron donation from cage to ring.<sup>2</sup>

(4) Reported in part: (a) K. M. Harmon, A. B. Harmon, and B. C. Thompson, *J. Amer. Chem. Soc.*, **89**, 5309 (1967); (b) K. M. Harmon, A. B. Harmon, T. Y. Susskind, B. C. Thompson, D. P. Ryan, and T. T. Coburn, Abstracts, 161st National Meeting of the American Chemical Society, Los Angeles, Calif., April 2, 1971, No. ORGN-183.

(5) To whom inquiries should be addressed at Oakland University.

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(7) A. B. Harmon and K. M. Harmon, *J. Amer. Chem. Soc.*, **88**, 4093 (1966).

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(10) The *x* indicates position of substitution not known.