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Carboranes. III. Reactions of the Carboranes

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The reactions of the carboranyl polyhedron and its influence on the chemistry of organofunctional substituents were investigated. Convenient laboratory syntheses for carborane, 1-methylcarborane, and some functional derivatives were developed. An unusual rearrangement in a Grignard reagent was observed. Metalation, amination, solvolytic degradation, and other reactions of these novel compounds were studied.

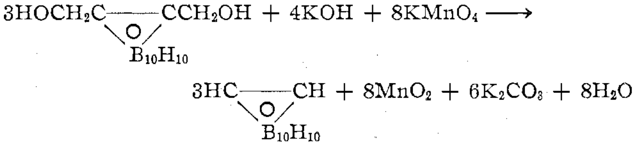
Carboranes containing alkyl, aryl, ether, ester, haloalkyl, and olefinic substituents can be prepared directly from decaborane and a suitably substituted alkyne.[1,2] More reactive functional derivatives such as carboxylic acids, carbinols, and epoxides cannot be prepared yet by this method. Good laboratory procedures are therefore desirable for substitution or modification of the functional groups on available carboranes. Such procedures are reported herein.

Preliminary studies[1,2] had already indicated that the carborane polyhedron would add two equivalents of the blue alkali metal–amine solutions, that it deactivated the olefinic bond in 1-isopropenylcarborane to certain ionic addition reactions, and that the ester functions in 1,2-bis-(acetoxymethyl)-carborane could be saponified and transesterified[2,3] in the normal way. Aside from its high oxidative and hydrolytic stability, little else was known about the reactivity of the polyhedron or its influence upon the chemistry of organofunctional substituents.

This paper presents the syntheses and reactions which were observed during the course of this study and further defines the nature of the interaction of the polyhedron with organofunctional substituents.

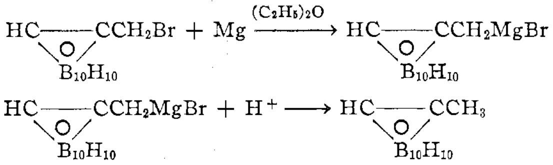
Discussion

Early in this work it was discovered that 1,2-bis-(acetoxymethyl)-carborane and its hydrolysis product, 1,2-bis-(hydroxymethyl)-carborane, could be oxidized by aqueous alkaline permanganate to give good yields of carborane. The oxidation of the diol proceeded rapidly at room temperature. The diester reacted much more slowly, its oxidation probably being dependent on a prior saponification step. The formation of carborane in this reaction was noteworthy in that it again demonstrated the stability of the carborane polyhedron to oxidizing and mildly alkaline environments. This stability against oxidation was observed with chromic acid,[4] acyl peroxides, hypochlorous acid, and other oxidants; stability against reduction with lithium aluminum hydride[4] and other reductants was also noted. 1-Methylcarborane was unattacked by permanganate, either in aqueous suspension or in pyridine solution. In our hands, the oxidation of 1,2-bis-(hydroxymethyl)-carborane became the method of choice for the preparation of carborane. This product is superior in quality to the carborane prepared from acetylene and bis-(diethyl sulfide)-decaborane, in that the latter product is difficult to obtain sulfur-free.



$$3HOCH_2C\underset{\underset{B_{10}H_{10}}{\diagdown O \diagup}}{\text{———}}CCH_2OH + 4KOH + 8KMnO_4 \longrightarrow 3HC\underset{\underset{B_{10}H_{10}}{\diagdown O \diagup}}{\text{———}}CH + 8MnO_2 + 6K_2CO_3 + 8H_2O$$

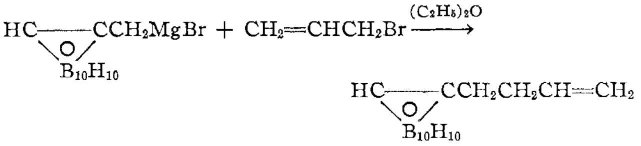
A valuable synthetic intermediate was realized when it was observed that 1-bromomethylcarborane[2] formed a "normal" Grignard reagent, 1-carboranylmethylmagnesium bromide, in ethyl ether. This Grignard reagent could be used for the preparation of 1-carboranylmethyl derivatives, but it also served as a source for methylcarborane. Like the oxidative synthesis of carborane, the hydrolysis of the Grignard reagent was a more convenient laboratory method than the direct propyne–Lewis base–decaborane interaction for the synthesis of methylcarborane.



$$HC\underset{\underset{B_{10}H_{10}}{\diagdown O \diagup}}{\text{———}}CCH_2Br + Mg \xrightarrow{(C_2H_5)_2O} HC\underset{\underset{B_{10}H_{10}}{\diagdown O \diagup}}{\text{———}}CCH_2MgBr$$

$$HC\underset{\underset{B_{10}H_{10}}{\diagdown O \diagup}}{\text{———}}CCH_2MgBr + H^+ \longrightarrow HC\underset{\underset{B_{10}H_{10}}{\diagdown O \diagup}}{\text{———}}CCH_3$$

Allyl bromide reacted with the Grignard reagent in ethyl ether to yield 4-(1-carboranyl)-1-butene.



$$HC\underset{\underset{B_{10}H_{10}}{\diagdown O \diagup}}{\text{———}}CCH_2MgBr + CH_2{=}CHCH_2Br \xrightarrow{(C_2H_5)_2O} HC\underset{\underset{B_{10}H_{10}}{\diagdown O \diagup}}{\text{———}}CCH_2CH_2CH{=}CH_2$$

However, when this same reaction was conducted in tetrahydrofuran, the product was shown to be 1-allyl-2-methylcarborane. Thus, 1-carboranylmethylmagnesium bromide had isomerized to 1-methyl-2-carboranylmagnesium bromide. This unusual rearrangement was an early indication that the hydrogen atoms attached to polyhedral carbon are sufficiently

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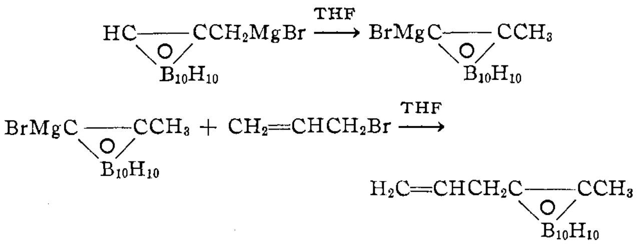
[1] M. M. Fein, J. Bobinski, N. Mayes, N. Schwartz, and M. S. Cohen, *Inorg. Chem.*, **2**, 1111 (1963).

[2] M. M. Fein, D. Grafstein, J. E. Paustian, J. Bobinski, B. M. Lichstein, N. Mayes, N. N. Schwartz, and M. S. Cohen, *ibid.*, **2**, 1115 (1963).

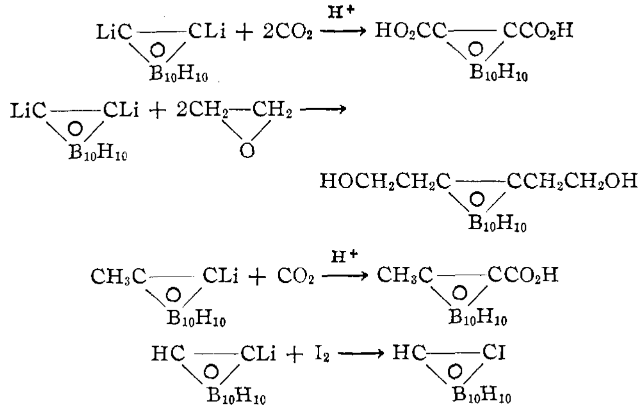
[3] J. E. Paustian, *et al.*, to be published.

[4] D. Grafstein, J. Bobinski, J. Dvorak, J. E. Paustian, H. F. Smith, S. Karlan, C. Vogel, and M. M. Fein, *Inorg. Chem.*, **2**, 1125 (1963).

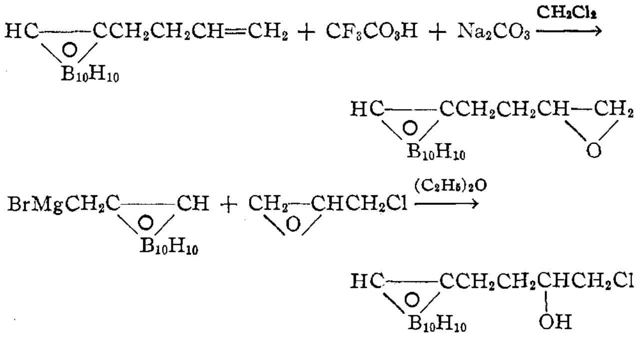
labile to permit metalation. These alkylation isomers are distinguished in the infrared mainly by the presence of the polyhedral C–H at 3060 cm.$^{-1}$ in 4-(1-carboranyl)-1-butene and its absence in 1-allyl-2-methylcarborane. The rearrangement of the Grignard reagent has been investigated[5] more thoroughly using a deuterium labeling technique and both Grignard reagents have been employed in the preparation of silane derivatives.



Various synthetic possibilities were suggested by the labile polyhedral C–H revealed by the Grignard rearrangement. However, attempts to form useful carboranyl Grignard reagents from carborane and methylcarborane were mainly unsuccessful. Negative Zerewitinoff reactions were observed in ethyl ether. However, in tetrahydrofuran solution, both carborane and methylcarborane gave essentially quantitative evolution of ethane with ethylmagnesium bromide. More reactive intermediates were obtained upon metalation with alkyl and aryllithium reagents. The carboranyllithium reagents thus produced frequently offer the most satisfactory intermediates to carboranyl acids, carbinols, and halides. For example, 1,2-carboranedicarboxylic acid, 1,2-bis-(hydroxyethyl)-carborane, 1-methyl-2-carboranylcarboxylic acid,[6] and 1-iodocarborane, were each prepared *via* a lithiated intermediate.



Reactions of Alkenylcarboranes.—Isopropenylcarborane can be catalytically hydrogenated over platinum, palladium, or Raney nickel, and it reduces potassium permanganate in acetone.[1] However, alkenylcarboranes, in general, are quite unreactive to cationic reagents, particularly when the polyhedron and the double bond are separated by decreasing numbers of methylene groups. Thus bromine in carbon tetrachloride added to the olefinic bond in 4-(1-carboranyl)-1-butene, but similar reactions were not observed with 1-allyl-2-methylcarborane, isopropenylcarborane,[1] or vinylcarborane. The carborane nucleus inhibited reactions of these olefinic substituents with hydrogen peroxide, peracetic acid, hypochlorous acid, or iodine monobromide in glacial acetic acid. Both isopropenyl- and butenylcarboranes were attacked by trifluoroperacetic acid. A stable epoxide was obtained from isopropenylcarborane, whereas this same reagent converted 4-(1-carboranyl)-1-butene to a glycol trifluoroacetate adduct. This difference is attributed to the more effective deactivating influence of the adjacent carboranyl polyhedron in isopropenylcarborane on acid-catalyzed epoxy ring opening. A chlorohydrin derivative of 4-(1-carboranyl)-1-butene was prepared indirectly by the reaction of epichlorohydrin in ether with 1-carboranylmethylmagnesium bromide. Under alkaline conditions, trifluoroperacetic acid converted 4-(1-carboranyl)-1-butene to an epoxide.



Reactions of Acids, Esters, and Carbinols.—1,2-Carboranedicarboxylic acid was surprisingly difficult to synthesize. Dimethyl 1,2-carboranedicarboxylate could be prepared from dimethyl acetylenedicarboxylate,[1] and it was seemingly an easy route to the diacid; however, it resisted hydrolysis. The diester was unattacked by refluxing concentrated hydrochloric acid, glacial acetic acid, and trifluoroacetic acid as well as several other acidic reagents. Unlike most carborane derivatives, the diester was unstable in alcoholic media. In aqueous dioxane, it formed a potassium salt with potassium hydroxide. Acidification gave an acidic product which no longer possessed a typical carborane spectrum, although the carbomethoxy groups were still intact. Successful saponification of the diester was achieved with cold 50% aqueous potassium hydroxide, but the reaction was slow and the yield of diacid was poor. This resistance to a carbonyl addition reaction is surprising in view of the strong electron-withdrawing character of the carborane polyhedron, suggested by the resistance of the alkenylcarboranes to cationic attack.

1,2-Carboranedicarboxylic acid resisted esterification, even under strong acid catalysis. A similar resistance to esterification is reported[4] for the related diacid, bis-(2-carboxy-1-carboranylmethyl) ether. In both cases, polyesterification could be effected only through a diacid halide intermediate.[7] Basic permanganate completely degraded 1,2-carboranedicarboxylic

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[5] N. Schwartz, *et al.*, to be published.

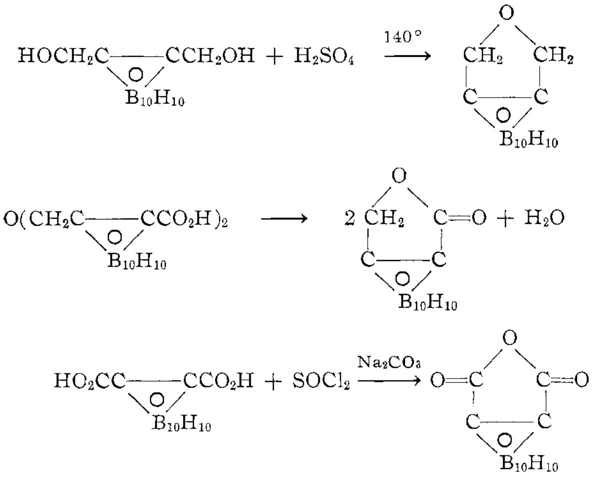
[6] D. Grafstein and J. Dvorak, *Inorg. Chem.*, **2**, 1128 (1963).

[7] J. Green, *et al.*, *J. Polymer Sci.*, to be published.

acid to boric acid. Carborane was not detected in the oxidation products.

Carboranylmethylmalonates also displayed a surprising stability to acid-catalyzed reactions. Thus, diethyl bis-(carboranylmethyl)-malonate[2] failed to transesterify with refluxing 1-butanol containing some *p*-toluenesulfonic acid, and it was recovered unchanged from 6 days of stirring with concentrated sulfuric acid at room temperature. Alcoholic potassium hydroxide and hot 50% aqueous potassium hydroxide caused the decomposition of this carborane. Saponification was slowly accomplished with 50% aqueous potassium hydroxide at room temperature. Acidification of the resulting salt gave a hygroscopic malonic diacid, which lost carbon dioxide on heating to give bis-(1-carboranylmethyl)-acetic acid. In the same way, 1-carboranylmethylmalonic acid was prepared from its diethyl ester.

A strong tendency to form 1,2-exocyclic derivatives was observed with disubstituted carboranes. 1,2-Bis-(hydroxymethyl)-carborane produced a volatile ether with sulfuric acid. A lactone[4] was formed from the pyrolysis of bis-(2-carboxy-1-carboranylmethyl) ether and a cyclic anhydride was formed from 1,2-carboranedicarboxylic acid with a variety of dehydrating reagents. In view of the stability of dimethyl 1,2-carboranedicarboxylate to saponification, the tendency to form 1,2-exocycles suggests that an important steric factor is operating in disubstituted carboranes.[6] Five-atomed exocycles have also been isolated.[7] A cyclic formal sublimed from an attempted polymerization of 1,2-bis-(hydroxymethyl)-carborane with trioxane and a cyclic phosphate was produced with polyphosphoric acid.



Reactions of Halomethylcarboranes.—Despite the facile formation of a Grignard reagent, the bromine atom in 1-bromomethylcarborane was quite unreactive. It was not easily displaced by nucleophilic reagents. Quaternization with triethylamine or hexamethylenetetramine did not occur (see below) and halogen exchange with sodium iodide in refluxing methyl ethyl ketone proceeded to only a modest extent. Halogen displacement reactions were not observed with sodium diethylmalonate, sodium acrylate, or sodium methacrylate. Only unchanged 1-bromomethylcarborane was recovered from an attempted condensation with allylmagnesium bromide. Similarly, 1,2-bis-(chloromethyl)-carborane[2] did not react with potassium cyanide in refluxing dimethyl sulfoxide or refluxing acetonitrile nor with cuprous cyanide in refluxing xylene. These observations can be rationalized by a strong electron-withdrawing inductive character for the carborane polyhedron.

Reactions of the Carborane Polyhedron.—Simple carboranyl compounds are inert to many nucleophilic reagents; alcohols, ethers, nitriles, sulfides, and weakly basic amines. However, in the course of this work, stable addition compounds were observed with certain amines. Addition products were obtained when carborane was treated with *n*-propylamine, piperidine, and hydrazine. Weaker bases such as aniline, pyridine, and ammonium hydroxide did not react. Steric factors may play a part since diethylamine, another strong base, also failed to react.

Thus far, the evidence suggests that the amine products are coordinate-covalent adducts and not lower boron-containing species. The reactions proceeded rapidly at room temperature in benzene or in bulk. Hydrogen was usually evolved, but in most cases, gas evolution did not exceed 0.1 mole per mole of carborane. Hydrogen evolution may be associated with a competing degradation reaction. When heptane solutions of carborane and a suitable amine were mixed, the product separated after a few minutes.

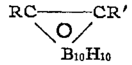
The *n*-propylamine product is a liquid at room temperature and both it and the solid piperidine product, m.p. 171–176°, are benzene-soluble. The carboranyl C–H band at 3060 cm.$^{-1}$ does not appear in the infrared spectra of these compounds. However, the observed shift of the BH absorption to 2500 cm.$^{-1}$ and the disappearance of the typical carborane band at 714 cm.$^{-1}$ imply that the nitrogen donor atoms are bonded directly to boron.

The stoichiometry of the reaction is less well defined. Ratios of N:B ranging from 1.5:10 to 3.3:10 were obtained initially. On purification, a tendency to converge on a value of 2:10 was noted. One sample of the carborane–*n*-propylamine adduct as initially prepared had an N:B ratio of 1.5:10; this was increased to 1.8:10 by the removal of volatile material, probably unreacted carborane, under vacuum. The N:B ratio of the carborane–piperidine adduct, initially 2.52:10, was decreased by two successive recrystallizations from benzene to 2.24:10 and then to 2.18:10. Best analyses of these and other diadducts are shown in Table I.

A number of adducts were observed between aliphatic amines and substituted carboranes. *n*-Propylamine reacted with 1-methylcarborane to give a 2:1 adduct, but isopropylamine and propargylhydrazine did not react. Refluxing aqueous triethylamine converted dimethyl 1,2-carboranedicarboxylate to an ether-insoluble solid, m.p. 112–114°. Infrared analysis indicated the formation of a B–N type adduct and

TABLE I

ANALYSES OF (AMINE)$_2$-CARBORANYL ADDUCTS


$RC\!-\!CR'$ (O) $B_{10}H_{10}$

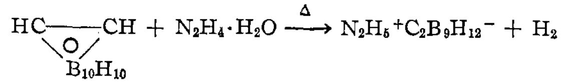
R	R'	Amine	% C Theory	% C Found	% H Theory	% H Found	% B Theory	% B Found	% N Theory	% N Found
H	H	*n*-Propylamine	36.60	32.74	11.52	10.84	41.21	40.24	10.67	9.44
CH_3	H	*n*-Propylamine	39.08	37.59	11.66	11.56	39.12	36.05	10.13	10.42
H	H	Piperidine	45.81	45.11	10.89	10.77	34.39	30.37	8.91	9.93
H	H	Piperidine	45.81	46.21	10.89	10.94	34.39	32.17	8.91	9.06
CH_3O_2C	CO_2CH_3	Isopropylamine	38.07	36.5	9.05	9.1	28.57	28.5	7.40	8.7
H	CH_2Br	$(CH_2)_6N_4$	34.80	32.62	7.14	7.89	20.9	23.54	21.64	19.01[a]

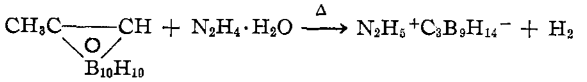
[a] Theory Br, 15.44; found Br, 13.88.

confirmed that the ester function was unchanged. An exothermic reaction was also observed with isopropylamine, giving a solid, m.p. 110–115°. 1-Bromomethylcarborane formed a B–N adduct with hexamethylenetetramine, rather than a quaternary salt.

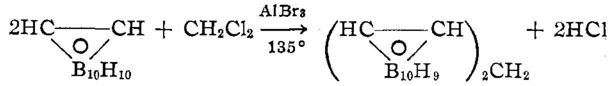
1,2-Bis-(hydroxymethyl)-carborane was treated with a series of amines and amides. With concentrated ammonium hydroxide, the solid diol was converted to an immiscible dense oil at 80°. Upon cooling, the oil solidified and after work-up with water, pure diol was recovered. Triethylamine in benzene converted the diol into a white solid, m.p. 180–185°, which crystallized from benzene. The spectra of the product indicated a complex adduct with B–N and ether linkages. Urea and the diol reacted rapidly in bulk with the evolution of ammonia. An insoluble, infusible solid was obtained whose infrared spectrum showed a cyclic ether structure and urea. Similarly, an insoluble, infusible solid was obtained with acetamide.

During the course of this investigation, Hawthorne[8] characterized the water-soluble products derived from the treatment of carborane and its derivatives with strong caustic solutions as salts of dicarbaundecaboranes. In this laboratory it was observed that hydrazine hydrate degraded carborane and methylcarborane to hydrazinium salts of dicarbaundecaborane and methyldicarbaundecaborane, respectively. Hydrazine hydrate degradation appears to be quantitative and much superior to other solvolytic reactions for the preparation of these anions.


$$\underset{B_{10}H_{10}}{HC\!-\!CH} + N_2H_4\cdot H_2O \xrightarrow{\Delta} N_2H_5{}^+C_2B_9H_{12}{}^- + H_2$$


$$\underset{B_{10}H_{10}}{CH_3C\!-\!CH} + N_2H_4\cdot H_2O \xrightarrow{\Delta} N_2H_5{}^+C_3B_9H_{14}{}^- + H_2$$

Both 1-isopropenylcarborane and 1-methylcarborane reacted with ethyl bromide and aluminum chloride in carbon disulfide to give polyalkylated products.[9] However, in our hands, carborane itself failed to demonstrate a similar reaction in carbon disulfide. Under drastic conditions, carborane and fused aluminum bromide (135–145°) reacted with methylene chloride, chloroform, and carbon tetrachloride. The methylene chloride product was an ether-soluble, clear, viscous gray-brown oil. From 62 to 89% of the total chlorine content was recovered as liberated hydrogen chloride. The product oil could be separated into a pentane-insoluble fraction, m.p. 138–152°, and a pentane-soluble fraction, m.p. 65–75°. The spectra and the negligible chlorine content indicated that both solids were complex mixtures of B-substituted dicarboranylmethanes. Spectrally similar pentane-insoluble solids were isolated from the chloroform reaction, m.p. 85–115°, and from carbon tetrachloride, m.p. 140–187°.


$$2\underset{B_{10}H_{10}}{HC\!-\!CH} + CH_2Cl_2 \xrightarrow[135°]{AlBr_3} \left(\underset{B_{10}H_9}{HC\!-\!CH}\right)_2CH_2 + 2HCl$$

Summary

Thus far, the chemistry of the carboranes can be interpreted as supporting a strong electron-withdrawing character for the polyhedron, which inductively deactivates olefinic substituents to ionic addition, inhibits nucleophilic displacement reactions on halomethyl derivatives, promotes metalation of polyhedral C–H, and enhances the acid strength[6] of carboxylic acid substituents. A potent steric factor can be implied from saponification and esterification studies as well as from the pronounced tendency to form 1,2-exocycles. The polyhedron is remarkably stable to oxidizing and reducing reagents and this permits selective oxidation–reduction reactions on organofunctional substituents. Polyhedral electron deficiency is evidenced by the formation of stable diadducts with strongly basic amines and by the addition of two equivalents of alkali metal in amine solution. Hydrolytic degradation is efficiently achieved with hydrazine hydrate but degradation in general becomes more facile in substituted carboranes, probably the result of combined steric and electronic factors. Friedel–Crafts alkylation occurs with difficulty, indicating that the polyhedron is too electron-deficient to promote substitution by electrophilic reagents.

Experimental

Carborane from 1,2-Bis-(hydroxymethyl)-carborane.—A suspension of 0.05 mole of 1,2-bis-(hydroxymethyl)-carborane in 100 ml. of 20% aqueous potassium hydroxide was stirred and the temperature kept at 20°. Finely powdered potassium permanganate (0.136 mole) was added at such a rate that there was no appreciable quantity of unreacted oxidant at any given time. The addition takes 1.5–2 hr. After the addition was completed, the reaction mixture was cooled and acidified. Considerable

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[8] M. F. Hawthorne, private communication.

[9] T. Neely, private communication.

foaming sometimes occurred, and 2 to 3 ml. of ether can be added from time to time to break the foam. The reaction mixture was then extracted with a total of 375 ml. of benzene. The benzene extracts were combined and dried. Evaporation of benzene and sublimation of the residue gave 4.18 g. (58% yield) of carborane.

An alternative isolation of carborane was often employed. After acidification, the mixture can be treated with sulfurous acid to dissolve all the manganese dioxide. Filtration of the resulting aqueous suspension gave a crude product in 75% yield. Carborane can then be purified by sublimation, but crystallization from a 1-butanol–heptane mixture gave highest purity carborane, m.p. 287–288°.

Carborane from 1,2-Bis-(acetoxymethyl)-carborane.—A mixture of 0.04 mole of 1,2-bis-(acetoxymethyl)-carborane and 200 ml. of 20% aqueous potassium hydroxide was stirred and the temperature maintained at 25°. Finely powdered potassium permanganate (0.107 mole) was added at such a rate that there was no appreciable quantity of unreacted permanganate in the reaction mixture at any given time. The addition takes 8–12 hr. After the addition was completed, the reaction mixture was cooled and neutralized with sulfuric acid. Considerable foaming occurred and 2 to 3 ml. of ether was added to break the foam. The reaction mixture was then extracted with a total of 250 ml. of benzene. The benzene extracts were combined and dried. Evaporation of benzene and sublimation of the residue gave 4.19 g. (73% yield) of carborane.

1-Methylcarborane.—1-Bromomethylcarborane (0.55 mole) in 100 ml. of sodium-dried ether was added at a fast dropwise rate to a refluxing, stirred mixture of 0.66 g.-atom of magnesium and 150 ml. of sodium-dried ether. The addition was complete in 2 hr. and the reaction mixture was refluxed for an additional 5 hr. The mixture, which was black in color, was then filtered free of unreacted magnesium using glass wool. A saturated water solution of ammonium chloride (100 ml.) was added dropwise to the filtrate. This resulted in an exothermic reaction which was controlled by the rate of addition of the ammonium chloride solution. Water (150 ml.) was slowly added to the reaction mixture. The ether layer was separated. Concentration of the solution gave crude 1-methylcarborane, m.p. 203–205°, which was recrystallized from ether to yield the pure product, m.p. 218–219°. The yield was 53 g. (60%).

4-(Carboranyl)-1-butene.—In one preparation, a Grignard reagent was prepared from 0.098 mole of 1-bromomethylcarborane and 0.098 g.-atom of magnesium in 250 ml. of ethyl ether. The Grignard reagent was filtered through glass wool. Allyl bromide (0.098 mole) in 80 ml. of ethyl ether was then added dropwise to the cooled (18°) Grignard solution. After refluxing the solution for several hours, hydrolysis was effected using a saturated aqueous ammonium chloride solution. The ether phase was separated and concentrated, and the product was distilled. A small amount of 1-methylcarborane sublimed at 70–80° (0.2 mm.) and then 12.1 g. (61% yield) of product distilled, b.p. 99–101° (0.2 mm.), m.p. 45–46°. The infrared spectrum confirmed the assigned structure.

Anal. Calcd. for $C_6H_{18}B_{10}$: B, 54.54. Found: B, 54.31.

1-Allyl-2-methylcarborane.—This reaction was run with the same quantity of reactants as above except that dry tetrahydrofuran was the solvent. Again, the temperature was maintained at 18° during addition of allyl bromide to the Grignard solution. The product was isolated by distillation, b.p. 100° (0.1 mm.), m.p. 17–18°, in 54% yield. The product, 1-allyl-2-methylcarborane, was identified by its infrared spectrum.

4-(Carboranyl)-1-butene Oxide.—Trifluoroacetic anhydride (0.04 mole) was slowly added over a 15-min. period to a mixture of 0.04 mole of 90% hydrogen peroxide and about 20 ml. of methylene chloride cooled by an ice–water bath. The solution obtained was stirred in the cold for 15 min. and then added over a 2-hr. period with stirring to a mixture of 12.0 g. of anhydrous sodium carbonate, 0.025 mole of 4-(1-carboranyl)-1-butene, and about 30 ml. of methylene chloride. During the addition, the mixture was kept at room temperature. Then the mixture was heated to reflux for 30 min., cooled, and filtered. 4-(1-Carboranyl)-1-butene oxide was isolated by distillation (3.4 g., 63% yield), b.p. 114° (0.1–0.2 mm.), 132–135° (0.4 mm.), m.p. 60–62°.

Anal. Calcd. for $C_6H_{18}B_{10}O$: C, 33.61; H, 8.46; B, 50.47. Found: C, 33.59; H, 8.62; B, 49.30.

4-(1-Carboranyl)-1,2-butyleneglycol Monotrifluoroacetate.—Omitting sodium carbonate in the above procedure gave 2.3 g. (30% yield) of the glycol monotrifluoroacetate, b.p. 148–150° (0.1 mm.).

Anal. Calcd. for $C_8H_{19}B_{10}F_3O_3$: F, 17.25. Found: F, 17.19.

4-(1-Carboranyl)-1-chloro-2-butanol.—Epichlorohydrin was added dropwise to an ethereal solution of 1-carboranylmethylmagnesium bromide. An exothermic reaction was observed. Upon work-up of the mixture, the desired chlorohydrin was obtained as a colorless viscous liquid, b.p. 135–145° (0.1 mm.), in 71% yield.

Anal. Calcd. for $C_6H_{19}B_{10}OCl$: Cl, 14.13. Found: Cl, 13.3.

1,2-Carboranedicarboxylic Acid from Carborane.—A solution of 10.0 g. of carborane in 200 ml. of dry tetrahydrofuran was added dropwise in 5 min. to 0.154 mole of butyllithium in heptane–pentane (1.5 *M*) at 0–10°. The mixture was stirred for 0.5 hr. and then gaseous carbon dioxide was passed through the liquid at 0–10°. The tetrahydrofuran solvent was removed by distillation and replaced by 200 ml. of benzene. Hydrogen chloride-saturated benzene (100 ml.) was added cautiously and finally anhydrous hydrogen chloride was passed through the mixture. The mixture was refluxed and the benzene was decanted. This acidification procedure was repeated on the solid residue and the benzene solutions were combined. Evaporation of benzene and crystallization from ethylene chloride gave 3.55 g. (24% crude yield) of 1,2-carboranedicarboxylic acid, m.p. 215–218°. Fractional recrystallization brings the melting point up to 225°.

1,2-Carboranedicarboxylic Acid from Dimethyl-1,2-carboranedicarboxylate.—Dimethyl 1,2-carboranedicarboxylate (0.011 mole) was treated with 0.053 mole of potassium hydroxide in 3 ml. of water at room temperature over a period of 3 hr. The dipotassium salt thus obtained was dried by azeotropic distillation, suspended in anhydrous benzene, and acidified with gaseous hydrogen chloride. The mixture was filtered and the filtrate concentrated to yield 0.8 g. (28% yield) of 1,2-carboranedicarboxylic acid. The product was recrystallized from ethylene chloride and melted at 223–225°.

Anal. Calcd. for $C_4H_{12}B_{10}O_4$: C, 20.68; H, 5.21; neut. equiv., 116. Found: C, 21.60; H, 6.43; neut. equiv., 124.

1,2-Bis-(hydroxyethyl)-carborane from Carborane.—Carborane (0.05 mole) was treated with 0.14 mole of phenyllithium in 300 ml. of ether. An ether solution containing approximately 0.2 mole of ethylene oxide was added at room temperature and the mixture was allowed to stand for 24 hr. Work-up in the usual way gave 4 g. (35%) of 1,2-bis-(hydroxyethyl)-carborane, m.p. 124–125°.

1-Iodocarborane.—The butyllithium reagent (0.15 mole) was added to a solution of 0.15 mole of carborane in 550 ml. of anhydrous ethyl ether maintained at −5°. Iodine (0.15 mole) was added slowly at −5° and the mixture was maintained at 5° for 3 hr. The reaction appeared to stop after 75% of the iodine had been added. Work-up of the mixture gave 23.60 g. (64%) of a solid, m.p. 131–136°.

Anal. Calcd. for $C_2H_{11}B_{10}I$: C, 8.88; H, 4.07. Found: C, 9.61; H, 4.02.

1-Carboranylmethylmalonic Acid.—Diethyl (1-carboranylmethyl)-malonate[2] (0.015 mole) was treated with 0.089 mole of potassium hydroxide in 5 ml. of water over a period of 24 hr. at room temperature. The dipotassium salt of (1-carboranylmethyl)-malonic acid thus obtained was dried thoroughly by azeotropic distillation with benzene, filtered, and suspended in ethyl ether. Dry gaseous hydrogen chloride was passed into the ether suspension and the potassium chloride formed was removed by filtration. After concentration of the ether solution, 3.3 g. of (1-carboranylmethyl)-malonic acid was obtained (80% yield). The product was recrystallized from benzene and melted at 146–147°.

Anal. Calcd. for $C_7H_{18}B_{10}O_4$: C, 30.64; H, 6.61; B, 39.43; neut. equiv., 137.2. Found: C, 30.31; H, 7.29; B, 39.18; neut. equiv., 143.5.

Bis-(1-carboranylmethyl)-malonic Acid.—Saponification of diethyl bis-(1-carboranylmethyl)-malonate[2] (0.08 mole), m.p. 198–199°, was accomplished in benzene solution using 40 g. of 50% aqueous potassium hydroxide at room temperature. Then 12.7 g. of the dipotassium salt was isolated by filtration, dried by azeotropic distillation in benzene suspension, and acidified with hydrogen chloride. Bis-(1-carboranylmethyl)-malonic acid, 1.9 g., was isolated as a white hygroscopic solid, decomposing at 65–70°. Decarboxylation was observed in refluxing toluene.

Anal. Calcd.: neut. equiv., 416 and 208. Found: neut. equiv., 400 and 227.

Cyclic Ether from 1,2-Bis-(hydroxymethyl)-carborane.—A mixture of 0.05 mole of the diol and 55 ml. of concentrated sulfuric acid was heated at 135–140° for 5 hr. During this period 7.57 g. (81.2% yield) of the product sublimed from the reaction media at atmospheric pressure. The white solid, m.p. 259.5–260.5° (sealed tube), showed CH_2OCH_2 at 1170 cm.$^{-1}$, CH at 2870 cm.$^{-1}$, BH at 2550 cm.$^{-1}$, and another peak at 1070 cm.$^{-1}$ in its infrared spectrum. No hydroxyl peak was evident.

Hydrazinium Methyldicarbaundecaborane.—A mixture of 0.010 mole of 1-methylcarborane and 20 ml. of hydrazine hydrate was heated at reflux for 3.5 hr. During this period some 440 ml. (98%) of gas at STP, identified by mass spectroscopy as pure hydrogen, was liberated. Evaporation of the solvent then gave 2.22 g. of methyldicarbaundecaborane salt. The product was extracted with ethyl ether and the residue, which decomposes at 198°, was dissolved in water and precipitated as a tetramethylammonium salt for analytical purposes.

Anal. Calcd. for $C_7H_{26}B_9N$: C, 37.93; H, 11.82; B, 43.92; N, 6.35. Found: C, 36.31; H, 12.13; B, 43.97; N, 6.40.

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CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, REACTION MOTORS DIVISION,
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Carboranes. IV. Chemistry of Bis-(1-carboranylalkyl) Ethers

BY DANIEL GRAFSTEIN, JACK BOBINSKI, JOSEPH DVORAK, JOHN E. PAUSTIAN,
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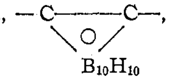
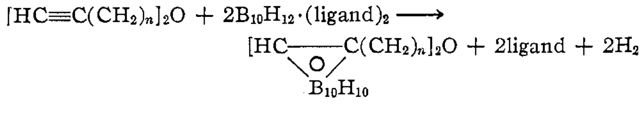
The carborane unit,  $\underset{B_{10}H_{10}}{\underset{\diagdown O \diagup}{-C{-}{-}{-}C-}}$, is exceptionally inert, and the chemical reactions of carboranes are limited principally to those of attached functional groups. The syntheses of two symmetrical dicarboranyl ethers are described. The lability of the 1-carboranyl hydrogen has been utilized to prepare several hydroxylic and carboxylic derivatives. The pyrolysis of the dicarboxylic acid, bis-(2-carboxy-1-carboranylmethyl) ether, gives rise to the lactone of 1-hydroxymethyl-2-carboranylcarboxylic acid.

In the initial paper of this series[1] the reaction of substituted acetylenes with 6,9-bis-(acetonitrile)-decaborane, $(CH_3CN)_2B_{10}H_{12}$, was described. The resulting carboranes, $B_{10}H_{10}C_2RR'$, were distinguished by unusual stability of the boron cage unit. In this paper are reported the results of an extension of this study to the synthesis, characterization, and reactions of dicarborane ethers and related difunctional derivatives.

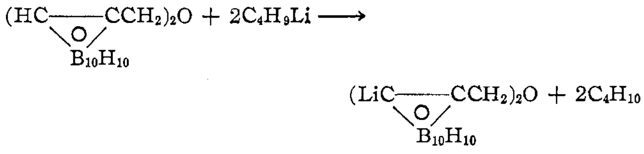
Propargyl and 3-butynyl ethers interacted with 6,9-bis-(acetonitrile)-decaborane to yield, respectively, bis-(1-carboranylmethyl) ether and β,β'-bis-(1-carboranyl)-diethyl ether, according to the equation



$$[HC{\equiv}C(CH_2)_n]_2O + 2B_{10}H_{12}\cdot(\text{ligand})_2 \longrightarrow [\underset{B_{10}H_{10}}{\underset{\diagdown O \diagup}{HC{-}{-}{-}C}}(CH_2)_n]_2O + 2\text{ligand} + 2H_2$$

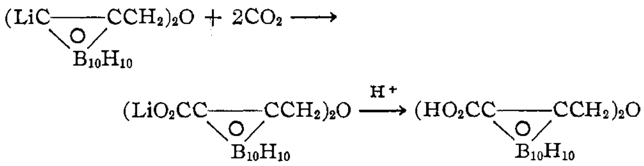
where $n = 1$ or 2. Yields were influenced by the nature of the ligand; the yield of the ether product, for example, was increased from 20% for the acetonitrile to 59% when 6,9-bis-(diethyl sulfide)-decaborane was used.

The dicarborane ethers showed the same stability characteristics of the borane unit as the parent carboranes. Hydrogen atoms attached to polyhedral carbon atoms of the new ethers were labile, like those of the parent carboranes, and their displacement by reaction with butyllithium formed the basis for the preparation of several interesting derivatives.



$$(\underset{B_{10}H_{10}}{\underset{\diagdown O \diagup}{HC{-}{-}{-}C}}H_2)_2O + 2C_4H_9Li \longrightarrow (\underset{B_{10}H_{10}}{\underset{\diagdown O \diagup}{LiC{-}{-}{-}C}}H_2)_2O + 2C_4H_{10}$$

Carbonation of the dilithio derivative in tetrahydrofuran gave a salt which upon acidification formed the diacid, bis-(2-carboxy-1-carboranylmethyl) ether, in high over-all yield.



$$(\underset{B_{10}H_{10}}{\underset{\diagdown O \diagup}{LiC{-}{-}{-}C}}H_2)_2O + 2CO_2 \longrightarrow (\underset{B_{10}H_{10}}{\underset{\diagdown O \diagup}{LiO_2CC{-}{-}{-}C}}H_2)_2O \xrightarrow{H^+} (\underset{B_{10}H_{10}}{\underset{\diagdown O \diagup}{HO_2CC{-}{-}{-}C}}H_2)_2O$$

When only one equivalent of butyllithium was used, bis-(1-carboranylmethyl) ether was converted to the monolithium derivative, which upon carbonation and acidification gave the monobasic acid.

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[1] M. M. Fein, J. Bobinski, N. Mayes, N. Schwartz, and M. S. Cohen, *Inorg. Chem.*, **2**, 1111 (1963).