

UNCLASSIFIED

AD 419686

DEFENSE DOCUMENTATION CENTER

FOR

SCIENTIFIC AND TECHNICAL INFORMATION

CAMERON STATION, ALEXANDRIA, VIRGINIA



UNCLASSIFIED

NOTICE: When government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related government procurement operation, the U. S. Government thereby incurs no responsibility, nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.

419686

(5) 667 900

OFFICE OF NAVAL RESEARCH

(15) Contract Nonr 3395(00)

(17) Task No. NR 356431

(14) TECHNICAL REPORT, NO. 15

(16) A New Series of Organoboranes. II. Carboranes from the Reaction of Decaborane with Acetylenic Compounds,

by

T. L. Heying, J. W. Ager, Jr., S. L. Clark, D. J. Mangold,
H. L. Goldstein, M. Hillman, R. J. Polak, and J. W. Szymanski

Prepared for Publication
in
Inorganic Chemistry

Olin Mathieson Chemical Corporation
Organics Division
New Haven, Connecticut

(11) JUNE 1963

Reproduction in whole or in part is permitted for
any purpose of the United States Government

DDC
OCT 1 1963
TISIA A

AD No. _____
DDC FILE COPY

419686

NO CUTS

Contribution from the Research Laboratories,
Organics Division, Olin Mathieson Chemical Corporation
New Haven, Connecticut

A New Series of Organoboranes. II. Carboranes
from the Reaction of Decaborane with Acetylenic Compounds

Received _____

By T. L. Heying¹, J. W. Ager, Jr.^{1a}, S. L. Clark, D. J. Mangold,
H. L. Goldstein^{1b}, M. Hillman^{1c}, R. J. Polak, and J. W. Szymanski^{1d}.

- (1) The authors wish to acknowledge the contributions of valuable experimental data by R. P. Alexander and J. A. Reid. Present addresses of authors no longer with this laboratory are 1a, Food Machinery and Chemical Corp.; 1b, Naval Propellant Plant; 1c, Brookhaven National Laboratory; 1d, United Aircraft Corp.

↓ Decaborane and certain of its derivatives reacted with acetylenic compounds in the presence of Lewis bases to produce members of a new class of organoboranes. The parent compound 11,12-dicarbadoecaborane (12) has the formula $B_{10}C_2H_{12}$ and various C and B substituted derivatives are reported. Unlike other higher boranes, this nucleus is quite impervious to attack by compounds containing active hydrogen nor does it attack reducible groups such as carbonyl or nitrile. ↑

Introduction

The reactions of decaborane with a variety of compounds of Lewis base classification have been described. One type of product from such reactions is the simple adduct² while a second type is typified by the compounds bis(diethylsulfide)decaborane³ and bis(chlorodiphenylphosphine)decaborane⁴, which are formed with the accompanying elimination of a molecule of hydrogen.

-
- (2) a. A. Stock and E. Pohland, Ber., 62B, 90 (1929);
b. W. H. Hill and M. S. Johnson, Anal. Chem., 27, 1300 (1955); c. S. J. Fitch and A. W. Laubengayer, J. Am. Chem. Soc., 78, 3546 (1956).
- (3) B. M. Graybill, J. K. Ruff and M. F. Hawthorne, J. Am. Chem. Soc. 83, 2669 (1961).
- (4) H. A. Schroeder, J. R. Reiner and T. L. Heying, Inorg. Chem. 1, 618 (1962).
-

The reaction products from pentaborane and various Lewis bases have been studied⁵ and recently, members of a novel series

-
- (5) A. B. Burg, J. Am. Chem. Soc. 79, 2129 (1957).
-

of organoboranes of the general empirical formula $B_n C_2 H_{n+2}$ have been prepared by the reaction of pentaborane with acetylene⁶.

-
- (6) R. E. Williams, C. D. Good and I. Shapiro, 140th A.C.S. Meeting, Chicago, Illinois, September 1961.
-

Consideration of these latter reactions along with the preparation and structure advanced for the anion and $B_{12}H_{12}^{-2}$ 7,8

-
- (7) A. R. Pitochelli and M. F. Hawthorne, J. Am. Chem. Soc., 82, 3228 (1960).
- (8) J. A. Wunderlich and W. N. Lipscomb, J. Am. Chem. Soc., 82, 4427 (1960).
-

prompted interest in the reactions of decaborane and its various derivatives with acetylenic compounds.

Longuet-Higgins and Roberts⁹ had demonstrated that the

-
- (9) H. C. Longuet-Higgins and M. deV. Roberts, Proc. Roy. Soc. A230, 110-119, (1955).
-

icosahedral structure as proposed for the $B_{12}H_{12}^{-2}$ ion requires 26 bonding electrons. The decaborane nucleus itself can contribute 24 such electrons and in the case in point, the twenty-fifth and twenty-sixth electrons are those present because of double negative charge of the anion. A neutral $B_{12}H_{12}$ species, therefore, is precluded by these considerations. It was postulated that if decaborane could react with acetylene, a stable entity similar to $B_{12}H_{12}^{-2}$ might form since the triple bond of acetylene could supply those electrons necessary for an icosahedral molecule. The icosahedral carborane structure which should arise from such a reaction was specifically predicted by Hoffman and Lipscomb¹⁰.

-
- (10) R. Hoffman and W. N. Lipscomb, J. Chem. Phys., 36, 3489 (1962).
-

Discussion

The reactions of decaborane and suitable derivatives with acetylenic compounds were investigated employing a variety of conditions. The formation of a new entity was first observed from the reactions of bis(acetonitrile)decaborane with acetylene in refluxing benzene. Hydrogen was evolved and a material was isolated which chemical analysis showed to have the empirical formula $B_{10}C_2H_{12}$. This formula was corroborated by mass spectral analysis. The more detailed elucidation of the structure of this new organoborane will be the subject of a later paper¹¹,

(11) Refer also to paper I of this series by H. A. Schroeder, T. L. Heying and J. R. Reiner, *Inorg. Chem.*, in press.

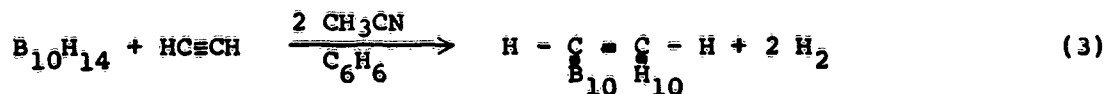
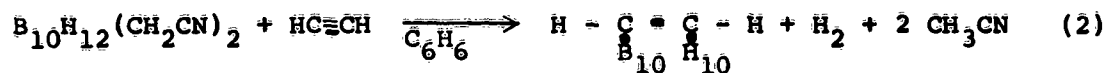
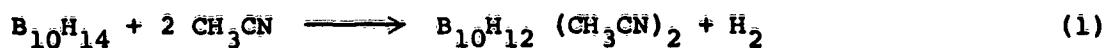
but from this structural determination it was ascertained that the material should be named 11,12-dicarbadoecaborane-12 since it has a closed icosahedral structure as in $B_{12}H_{12}^{-8}$ with the 11 and 12 boron atoms substituted for by two carbon atoms. This name is quite cumbersome, especially in the case of highly substituted compounds, and for brevity it is referred to as carborane¹² (carborane-12 where the numerical designation is necessary) since the material falls into the category of

(12) In writing descriptive formulae, the notation $\begin{array}{c} -C=C- \\ | \quad | \\ B_{10} \quad H_{10} \end{array}$

is used to denote the carboranyl group; thus carborane itself is $H - \begin{array}{c} C=C \\ | \quad | \\ B_{10} \quad H_{10} \end{array} - H$.

carboranes as described by Williams, et. al.⁶.

The yields of carborane were not good in the initial experiments, and during work toward improving them, it was found that use of the isolated nitrile or amide derivatives of decaborane was unnecessary since decaborane would react directly with acetylene in the presence of the nitrile or amide. Thus, reactions 1 and 2 were essentially combined as in reaction 3.



A study of reaction 3 was made by sampling at various time intervals and analyzing these samples mass spectrometrically. By plotting the concentrations of decaborane, acetonitrile (2 moles per mole of decaborane) and carborane versus time, it was readily seen that the nitrile was not required in stoichiometric amounts. To substantiate this, the quantity of acetonitrile used was decreased and it was found that reaction rate increased and the yield of carborane was greater when only one mole equivalent of nitrile was used. Reaction would proceed even when only 0.1 mole equivalent of acetonitrile was used and it was subsequently found that it was often advantageous to use approximately 0.9 mole acetonitrile per mole of decaborane.

In the initial stages of the investigation benzene was used as solvent but, having determined that the desired reaction was catalyzed by the presence of organic bases, it was postulated that the same effect could be obtained by merely using a solvent which itself is a mild Lewis base. This proved to be the case

as good yields of many carboranes were obtained by reacting decaborane with an acetylenic compound in tetrahydrofuran, diethyl ether or diethyl sulfide. In addition, it was found that diethyl sulfide could be used advantageously in place of acetonitrile in the reactions initially described.

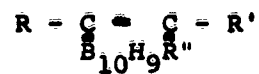
Of the solvents screened for use for the preparation of carboranes it was found that benzene, dialkyl ethers and dialkyl sulfides were the most useful. It was also found that the reaction does not proceed at a reasonable rate below 70°C, and, therefore it is necessary to use an autoclave when employing the low boiling solvents such as diethyl ether.

The solid products are white and crystalline while the liquids are clear and of rather high refractive index. The materials are quite stable at elevated temperatures and the carborane nucleus is inert to air, moisture and aqueous acids and alkalis. In fact, several compounds have been distilled from concentrated sulfuric acid without change. This behavior is in marked contrast to decaborane which is rather readily hydrolyzed and oxidized.

In addition to carborane itself, many C-alkyl and C-alkenyl derivatives were prepared by using the appropriate, substituted acetylene. Some symmetrical acetylenes such as 2-butyne or 3-hexyne would not react although unsymmetrical substituted acetylenes usually gave high yields of the corresponding carboranes. A summary showing the carboranyl hydrocarbons prepared by direct reaction of an acetylene with decaborane is given in Table I.

Table I

Carboranyl Hydrocarbons Made by Direct Synthesis



	R	R'	R''	M.P., °C (a)	Yield, %	B.P., °C
I	H	H	H	320	65-77	—
II	-CH ₃	H	H	114-5	—	—
III	-CH=CH ₂	H	H	78-79	65-70	—
IV	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{C}=\text{CH}_2 \end{array}$	H	H	45-46	70	—
V	n-C ₃ H ₇	H	H	62	—	—
VI	n-C ₄ H ₇	H	H	—	—	75/0.01
VII	-(CH ₂) ₂ CH(CH ₃) ₂	H	H	33	23	—
VIII	-C ₆ H ₅	H	H	66-67	27	—
IX	-nC ₆ H ₁₃	H	H	—	—	101-2/0.5
X	$\begin{array}{c} -(\text{CH}_2)_3-\text{C}=\text{CH} \\ \\ \text{B}_{10}\text{H}_{10} \end{array}$	H	H	355-357	—	—
XI	H	H	-C ₂ H ₅	—	77	-(b)

(a) Melting points were achieved on a Fisher-Johns apparatus and are uncorrected.

(b) Consult Experimental.

Some products derived from boron substituted decaboranes^{3,4} are also included.

(13) R. L. Williams, I. Dunstan and N. J. Blay, J. Chem. Soc.,
1960, 5006.

(14) Ibid., 5012.

This reaction of decaborane also occurred with many functionally substituted acetylenic compounds but, compounds such as propargyl alcohol or acetylenedicarboxylic acid preferentially led to the destruction of the borane structure rather than producing the desired carborane. Table II lists the preparations of those substituted carboranes which were achieved by the direct reaction of decaborane with the corresponding substituted acetylene.

Table II

Functionally Substituted Carboranes Prepared
By Direct Synthesis



	R	R'	Yield, %	M.P., °C	B.P., °C
XII	-CH ₂ Br	H	70	30	—
XIII	-COOCH ₃	H	35	73	—
XIV	-CH ₂ Cl	-CH ₂ Cl	74	119-120	—
XV	-CH ₂ OOCCH ₃	H	83	42-43	82-84/0.2 mm.
XVI	-nC ₃ H ₇	Br	66	44-45	107/1
XVII	-nC ₄ H ₉	Br (2)	37	—	85-90/0.5
XVIII	-(CH ₂) ₂ OOCCH ₃	H	72	61-63	146/1.6
XIX	-CH(OOCCH ₃)CH ₃	H (1)	66	—	85-95/0.2
XX	-CH ₂ N(C ₂ H ₅) ₂	H (3)	(4)	33-35	—
XXI	-CH ₂ OOCCH ₃ - CH ₂ OOCCH ₃		89	43-44	—
XXII	-COOCH ₃	COOCH ₃	54	66-67	—

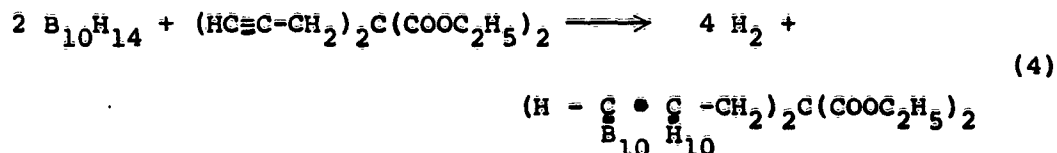
(1) nD²¹ = 1.5291

(2) nD²³ = 1.5500

(3) Hydrochloride m.p. > 300°C

(4) > 50%, but not all was recovered

The reaction was extended to the diacetylenic compound diethyl dipropargylcarbonate, and the corresponding dicarboranyl derivative (m.p. 199-202°C) was achieved in 55 percent yield according to reaction 4.



Experimental

Reagents: Unless specified to the contrary, reagents were used as received from various commercial sources. Decaborane was from the Olin Mathieson Chemical Corporation.

Analysis: The elemental analysis of the carboranes by standard techniques sometimes produced results which were not quite acceptable. Boron analyses (Parr Bomb method) were usually 1-2 percent lower than theoretical and this was found to be due to boron carbide formation. Carbon analyses were sometimes 1-2 percent higher than theoretical but, the cause of this has not been ascertained. By employing cumbersome techniques, accurate analyses could be obtained and are herein reported for fundamental compounds for which they were obtained¹⁵. It was

(15) Recently a new elemental analytical procedure has been reported which has proven very satisfactory for such compounds; R. C. Rittner and R. Culmo, Anal. Chem. in press.

found that mass spectrometric analysis of the reaction mixtures and products coupled with infrared analysis afforded an accurate means of identifying the carboranes and of establishing any impurities which were present. The method(s) of analysis in each instance is noted.

Carborane I. In a typical reaction, a 1-liter, three-necked flask is equipped with an efficient paddle stirrer, inlet tube reaching as near to the bottom of the flask as possible and an adapter for installing a second gas inlet and a water-cooled condenser. An acetylene source is connected to a purification train consisting of first a tower containing granular alumina, next a scrubber of concentrated sulfuric acid, then a tower of solid sodium hydroxide and finally the line is split to be attached in parallel to the two gas inlet tubes of the reaction vessel. In the flask a solution of 200 g. decaborane in 225 ml. di-n-propyl ether and 225 ml. diethyl sulfide is prepared. The flask and contents are heated at $40 \pm 5^\circ\text{C}$ for at least 12 hours and then heated to $90 \pm 5^\circ\text{C}$, at which temperature acetylene is admitted at a rapid rate for 24 hours. The mixture is cooled and the volatile materials are removed under reduced pressure. The solvents may be collected and re-used in succeeding preparations. The residue is dissolved by adding individually three 250-ml. portions of methanol and each portion is quickly poured into a 3-liter, three-necked flask equipped with a magnetic stirrer, water cooled condenser and an addition funnel. Provisions for cooling as needed are made. The mixture is stirred until the vigorous reaction has subsided (about 10 minutes) and cooling may be necessary. 200 ml. of concentrated hydrochloric acid is slowly added, with cooling to control the reaction, and the mixture allowed to stir for 30 minutes. Next, 100 ml. of acetone is added. A very vigorous reaction occurs initially but subsides after about 20 ml. has been added. The resulting mixture is allowed to stir overnight.

The mixture is poured into approximately 16 liters of water ($80-85^\circ\text{C}$) and after 30 minutes the yellow precipitate which has accumulated on the surface is removed and allowed to drain. The wet solid is next dissolved in 800 ml. methanol and a solution of 40 g. of sodium hydroxide, dissolved in a

minimum amount of water, is added with vigorous stirring. This solution is quickly poured into 3 liters of cold water, and the resulting precipitate is removed by filtration, washed with cold water and allowed to air-dry for 24 hours.

The product is ground to a powder and mixed with an equal amount of anhydrous calcium chloride and placed in a large soxhlet thimble for extraction with a liter of pentane for 24 hours. The pure white product crystallizes in the pentane extract. When the extraction is complete, the pentane may be decanted and used in succeeding preparations or evaporated to completely recover the product. By this procedure 153-180 g. of pure white carborane (65-77 percent yield) is obtained.

Anal.: Calc'd. for $B_{10}C_2H_{12}$: %B, 75.0; C, 16.7; H, 8.3

Found: %B, 74.9; C, 16.9; H, 8.4, 8.1

Through many experiments it has been found that carborane can be obtained in highest yield and purity suitable for any synthesis purpose by utilizing the method described. Smaller quantities may be purified by vacuum sublimation after the treatment with hydrochloric acid in methanol and acetone. Other less cumbersome modes of purification have resulted in poorer recovery and the product contained impurities which interfered with some subsequent reactions.

Methylcarborane II. A solution of 2.0 g. decaborane (0.016 mole) in 30 ml. of tetrahydrofuran was sealed in a 250-ml. autoclave. Without stirring, the autoclave was filled to 50 psig. with methylacetylene. Stirring was begun and the mixture was heated at 125°C for 5 hours. After cooling, the resulting solution was analyzed mass spectrometrically to show that it contained 0.7 percent unreacted decaborane and 4.4 percent of methylcarborane. The solvent was removed under reduced pressure and the residue (2.2 g.) was sublimed to give a product containing 12 percent decaborane and 88 percent methylcarborane. This

material was dissolved in pentane and the solution was treated with trimethylamine to precipitate the decaborane as its adduct which was removed. Evaporation of the pentane are pure methylcarborane as evidenced by its mass and infrared spectra.

Vinylcarborane III. In a typical experiment a 5-liter, 3-necked flask is equipped with a 500 ml. graduated, dropping funnel, a nitrogen inlet tube and a straight bore, water condenser topped by a dry ice condenser which is vented through a Nujol-filled trap. Agitation is achieved via a magnetic stirrer and the reactor is warmed by use of a suitable heating mantle. Decaborane (454 g.) ethyl sulfide (360 ml. or 0.9 mole/mole decaborane) and toluene (2700 ml.) are mixed thoroughly in the reactor and allowed to stand overnight under nitrogen. This mixture is then heated with stirring to (80-90°C) for one hour and the temperature is adjusted to 85°C whereupon 450 ml. of a cold solution of vinylacetylene in xylene (1:1 by weight) is added dropwise. The addition usually requires 1.5-2 hours to maintain the reaction temperature between 90 and 100°C. After the addition is complete, reflux is maintained for 1.5-2 hours and the mixture is allowed to cool and stand overnight. The apparatus is then arranged so that the bulk of the solvent may be evaporated with the aid of a water aspirator and this is continued until the volume becomes less than one liter. The solvents may be recovered and re-used. The remainder is transferred to a 1-liter flask fitted with a Claisen head to which is attached a series of detachable glass bulbs in which the product condenses and is collected. The mixture is distilled at 0.5-1.0 mm. of mercury until the flask temperature reaches 135-140°C. Vinylcarborane distills at 75-80°C at 0.5 mm. mercury. Yields of 65-70 percent of theoretical are obtained. The product as recovered is suitable for many synthesis purposes but, can be further purified as follows. The solid is dissolved in methanol and distilled water is added until, with gentle warming, solution is maintained. The solution is then cooled to 0°C and

the precipitated product is removed. If the filtrate is treated with additional water and the cooling repeated, essentially quantitative recovery of the product is achieved. Vinylcarborane treated in this manner melts at 78-79°C.

Isopropenyl Carborane IV.

A. A solution of 10 g. decaborane, 60 ml. ether, 4 ml. diethyl sulfide and 6.5 g. isopropenylacetylene was allowed to react in an autoclave at 95°C for 17 hours. The maximum pressure developed was 255 psig. After removal, the ether was distilled off and the residue was distilled at 100°C/1.0 mm. The distillate (11.5 g., 68 percent) crystallized and melted at 35-40°C and was found by mass spectrometric analysis to contain 98.5 mole percent isopropenylcarborane and 1.5 mole percent unreacted decaborane. Recrystallization of a small portion gave a white waxy solid melting at 45°C.

B. A solution of 10 g. decaborane, 60 ml. di-n-butyl ether and 4 ml. diethyl sulfide was allowed to stand overnight. It was next heated to boiling and 10 g. isopropenyl acetylene was added as fast as possible, but without causing excessive loss through its vaporization. After the addition is complete, it was allowed to reflux for one hour and cooled to room temperature, after which trimethylamine was passed through until no more precipitate formed. The mixture was filtered and the isopropenylcarborane was isolated as in method A. Yields of about 70 percent were achieved by this procedure.

Alkylcarboranes. Table I lists n-butylcarborane (VI), n-propylcarborane (V), n-hexylcarborane (IX) and 1,3-dicarboranylpropane (X). The following general procedure illustrates the method of preparation.

Decaborane, acetonitrile (0.9 moles/mole decaborane), and the acetylenic hydrocarbon (10 percent molar excess) are dissolved in benzene and refluxed until hydrogen evolution

subsides, or the production of the carborane can be followed by periodically examining a small sample of the reaction mixture mass spectrometrically. When the reaction is complete, the volatile materials are removed under reduced pressure. The resulting residue is dissolved in benzene and treated with trimethylamine until no more precipitate forms. The mixture is filtered, and the solvent and the carborane isolated by vacuum distillation (V, VI) or by crystallization from pentane (VII, XIV).

γ-Methylbutylcarborane (VII). A solution of 3 g. 5-methyl-1-hexyne and 5 g. bis(acetonitrile)decaborane in 50 ml. benzene was refluxed for 5 hours. The mixture was filtered and the filtrate treated with trimethylamine. The resulting mixture was also filtered, and the solvent was removed. Recrystallization are 23 percent γ-methylbutylcarborane as identified by its mass spectrum.

Phenylcarborane (VIII). Three grams of phenylacetylene and 5 g. bis(acetonitrile)decaborane in 50 ml. benzene was refluxed for two hours. After cooling and filtering, the filtrate was treated with trimethylamine and the resulting mixture was also filtered. On evaporation of the filtrate and recrystallization of the residue from pentane, phenylcarborane was obtained in 27 percent yield.

Anal.: Calc'd. for $B_{10}C_8H_{16}$: % B, 49.2; C, 43.6; H, 7.3

% B, 48.7; C, 44.4; H, 7.9

B-Ethylcarborane (XI). The preparation of B-ethylcarborane from monoethyldecaborane containing two isomers was conducted in at least twenty different manners. In all cases the product varied only in the ratio of the isomeric B-ethylcarboranes obtained. This could be ascertained through infrared and mass spectrometric analysis and was reflected in slight differences in refractive index. In general, di-n-butylether was found to be the best solvent for this reaction and di-n-propyl sulfide, di-n-butyl sulfide and n-butyl methyl sulfide were the desired

Lewis bases. With these materials, yields ranged from 70-83 percent. A typical experiment giving 77 percent yield is described.

A solution of 100 g. of ethyldecaborane in 84.4 g. n-butyl methylsulfide in 114.7 g. di-n-butyl ether is placed in a 1-liter, 3-necked flask equipped with a high speed, turbine-drive stirrer (5000 r.p.m.), water-cooled condenser and sintered glass, gas delivery tube reaching to near bottom of the flask. An oil bath is provided. The stirred mixture is slowly heated to 110°C and acetylene, purified as in the preparation of I, is admitted at a rate of 90 cc./minute for 8 hours. Initially, the reaction foams vigorously but after 2-3 hours subsides as the color changes from light yellow to burnt orange.

The mixture is cooled and the volatile materials are removed under reduced pressure. The residue is transferred to a 250-ml. flask, and, using a modified Claisen-type stillhead having a cold-finger condenser and liquid fractionating take-off, is distilled under reduced pressure. Distillation is allowed to proceed until the overhead temperature has risen from 70°C/0.3 mm. to 110°C/2.5 mm. The distillation is stopped to avoid decomposition of the sulfur-containing residue. The pot temperature is not allowed to go above 150°C. Redistillation gives 89.1 g. product distilling at 70°C/0.3 mm. (i.e. n_D^{25} 1.5375) while the bath temperature is maintained below 170°C.

By infrared and mass spectral analysis the product is identified as a mixture of two isomers of B-ethylcarborane.

Anal.: Calc'd. for $B_{10}C_4H_{17}$: % B, 62.8

Found: % B, 62.7, 62.8

Separation of the two isomers is partially achieved by careful fractionation.

bromomethylcarborane (XII). A solution of 10 g. (0.082 mole) of decaborane, 4 ml. (0.037 mole) of ethyl sulfide and 40 ml. of di-n-propyl ether was refluxed for one-half hour. The mixture was cooled to 70°C and 10 g. (0.083 mole) of propargyl bromide was added slowly. Hydrogen was evolved and the temperature rose to 85°C. The addition took about one hour. The mixture was then refluxed for 3 hours and allowed to stand overnight. The ether was removed under reduced pressure, and the product distilled at 80-85°C/0.6 mm. The yield was 13.9 g. (69.5 percent) of a clear liquid which readily solidified on standing. Recrystallization from pentane gave a white crystalline product which was identified by its mass spectrum.

Methyl Carboranecarboxylate (XIII). Four and one-tenth grams (0.02 mole) bis(acetonitrile)decaborane and an equimolar quantity of methylpropiolate were refluxed in 50 ml. of benzene for four hours. After filtering, the solvent was removed from the filtrate and the resulting semi-solid was transferred to a Soxhlet apparatus and extracted with pentane. A white solid is recovered from the extract and after recrystallization from pentane-ether melted at 73°C. Methyl carboranecarboxylate identified through its mass and infrared spectra was recovered in 35 percent yield.

bis-Chloromethylcarborane (XIV). Ten grams decaborane, 11. g. 1,4-dichlorobutene-2, 3 ml. diethyl sulfide and 40 ml. ethyl ether were placed in a 250 ml. autoclave and heated at 90°C for 8 hours. The maximum pressure was 320 psig. After cooling, the contents of the autoclave were removed, and the ether was evaporated. The residue was dissolved in pentane, filtered and the filtrate cooled in a dry-ice bath. The precipitated crystals were removed and recrystallized from pentane giving 14.5 g. (74 percent) of bis-chloromethylcarborane which was identified by its mass and infrared spectra.

Acetoxymethylcarborane (XV). Two grams (0.0164 mole) of decaborane was dissolved in 15 ml. of benzene, and to it was added an equimolar quantity of acetonitrile and 2.1 g. (0.021 mole) of propargyl acetate. The mixture was refluxed for 48 hours; gas evolution was vigorous at first, but later subsided. The resulting yellow solution was treated with trimethylamine to precipitate any excess decaborane. The solution was concentrated and the residue was distilled at 82-84°C/0.2 mm. giving 2.9 g. (83 percent) of a liquid which crystallized to a white solid on standing. The material was identified by mass spectrometric and infrared analysis as acetoxymethylcarborane.

C-Bromo-C'-n-propylcarborane (XVI). A solution of 14.7 g. 1-bromo-1-pentyne, 11.0 g. decaborane, 35 ml., 1,4-dioxane and 7 ml. diethyl sulfide was heated at 70-80°C for 1 hour in a 200-ml., round-bottom flask and then refluxed for two hours. When no more hydrogen was evolved, the dioxane was removed under reduced pressure. The residue was distilled in vacuo, collecting the fraction which distilled at 99-100°C/1.0 mm. **CAUTION:** Toward the end of this distillation the temperature will begin to rise noticeably. Remove the heat at this point or the residue will suddenly decompose causing rupture of the apparatus and consequent fire! The product was redistilled giving 25.0 g. (66 percent) of clear liquid which solidified on standing. It was identified by its mass spectrum.

C-Bromo-C'-n-butylcarborane (XVII). This was prepared in 37 percent yield by the method given previously for XVI. The product was a liquid distilling at 85-90°C/0.5 mm. The same precautions are advised in purifying this as were stated for the preparation of the n-propyl homolog.

β -Acetoxyethylcarborane (XVIII). A solution of 4.0 g. (0.0327 mole) of decaborane, 4.5 g. (0.0402 mole) 3-butny-1-yl acetate and 1.5 g. (0.037 mole) acetonitrile in 30 ml. benzene was refluxed for 103 hours. The solvent was removed and 5.17 g. (71.7 percent) of liquid which solidifies to a white solid distilled at 108-118°C/0.3 mm. Mass spectrometric and infrared analysis showed it to be essentially pure β -acetoxyethylcarborane.

Anal.: Calc'd. for: $B_{10}C_4O_2$: %C, 31.2; H, 7.88

Found: %C, 32.1, 31.7; H, 7.9, 8.4

α -Acetoxyethylcarborane (XIX). A solution of 4.0 g. (0.0327 mole) of decaborane, 4.5 g. (0.0402 mole) of 3-butyn-2-yl acetate and 1.5 g. (0.0366 mole) of acetonitrile in 30 ml. benzene was refluxed for 95 hours. The benzene was removed and the residue was distilled at 85-95°C/0.15-0.2 mm. to recover 4.75 g. (65.7 percent) of a slightly yellow liquid $n_D^{21} = 1.5291$. Mass spectrometric and infrared examination indicated it to be essentially pure α -acetoxyethylcarborane.

Anal.: Calc'd. for: $B_{10}C_6H_{18}O_2$: %C, 31.2; H, 7.88

Found: %C, 33.0; H, 7.81

N,N-Dimethylaminomethylcarborane (XX). A solution of 6.1 g. decaborane and 5.5 g. N,N-diethylamino-2-propyne in 50 ml. benzene was refluxed for 7.5 hours. After cooling, the mixture was filtered and the filtrate was extracted with dilute hydrochloric acid. The acid was neutralized and the amine which is released was recovered in ether. Isolation and recrystallization from pentane gives a waxy, white solid.

Anal.: Calc'd. for: $B_{10}C_7H_{23}N$:

% B, 47.15; C, 36.64; H, 10.1; N, 6.11

% B, 45.8; C, 37.1; H, 9.8; N, 6.4

bis(Acetoxymethylcarborane) (XXI). A mixture of 5 g. (0.041 mole) of decaborane, 8 g. (0.047 mole) of butyndiyl-1,4-diacetate and 2 ml. (0.0186 mole) diethylsulfide in 40 ml. of diethyl ether was placed in a 250 ml. autoclave and heated at 110°C for 4.5 hours. The mixture was cooled and the ether removed. The residue was dissolved in about 200 ml. of pentane, filtered and the filtrate was cooled in a dry-ice-acetone bath. The cooled solution was filtered to recover 10.5 g. of material which melted near room temperature. Several recrystallizations from pentane gave a white solid (m.p. 43-44°C) identified by mass spectrometric and infrared analysis as the desired compound.

Dimethyl Carboranedicarboxylate (XXII). A mixture of 18.0 g. bis(acetonitrile)decaborane, 15 g. dimethyl acetylenedicarboxylate and 50 ml. toluene was refluxed for 22 hours. The toluene was removed under reduced pressure and the residue was treated with pentane to extract the product. Recrystallization from pentane gave 12.5 g. (53.6%) of dimethyl carboranedicarboxylate. Mass spectral and infrared examination established the identity of the product.

Acknowledgments

This research was supported in large part by the United States Air Force under Contract AF 33(616)-5934 monitored by the Propulsion Laboratories, Air Force Flight Test Center, Edwards Air Force Base, California and partly by the Office of Naval Research. The authors are grateful for the assistance of Dr. J. H. Norman who interpreted the mass spectra, through which many of the compounds were initially identified, and who contributed many helpful suggestions.

TECHNICAL REPORT DISTRIBUTION LIST

CONTRACTOR OLIVATHILSON CHEMICALS CORPORATION

NR NO. 356-131

CONTRACT NUMBER Hour 335(00)

DATE 15 FEB 1962

<u>NO. COPIES</u>	<u>NO. COPIES</u>
Commanding Officer Office of Naval Research Branch Office The John Crerar Library Building 106 East Randolph Street Chicago 1, Illinois (1)	Air Force Office of Scientific Research (SRC-E) Washington 25, D. C. (1)
Commanding Officer Office of Naval Research Branch Office 346 Broadway New York 13, New York (1)	Commanding Officer Diamond Ordnance Fuze Laboratories Washington 25, D. C. Attn: Technical Information Office Branch 012 (1)
Commanding Officer Office of Naval Research Branch Office 1030 East Green Street Pasadena 1, California (1)	Office, Chief of Research & Development Department of the Army Washington 25, D. C. Attn: Physical Sciences Division (1)
Commanding Officer Office of Naval Research Branch Office Box 39 Navy #100 Fleet Post Office New York, New York (7)	Chief, Bureau of Ships Department of the Navy Washington 25, D. C. Attn: Code 342A (2) Code 634C (1)
Director, Naval Research Laboratory Washington 25, D. C. Attn: Technical Information Officer (6) Chemistry Division (2)	Chief, Bureau of Naval Weapons Department of the Navy Washington 25, D. C. Attn: Technical Library (3) Code RR:A-3 (1)
Chief of Naval Research Department of the Navy Washington 25, D. C. Attn: Code 425 (2)	ASTIA Document Service Center Arlington Hall Station Arlington 12, Virginia (10)
DDRL&E Technical Library Room 3C-128, The Pentagon Washington 25, D. C. (1)	Director of Research U.S. Army Signal Research & Development Laboratory Fort Monmouth, New Jersey (1)
Technical Director Research & Engineering Division Office of the Quartermaster General Department of the Army Washington 25, D. C. (1)	Naval Radiological Defense Laboratory San Francisco 24, California Attn: Technical Library (1)
Research Director Clothing & Organic Materials Division Quartermaster Research & Engineering Command U. S. Army Natick, Massachusetts (1)	Naval Ordnance Test Station China Lake, California Attn: Head, Chemistry Division (1) Code 40 (1) Code 50 (1)

REVISED 1 FEB 1962

TECHNICAL REPORT DISTRIBUTION LIST

Page 2

CONTRACTOR OLIN MATHIESON CHEMICALS CORPORATION

NR NO. 356-431

CONTRACT NUMBER Monr 3395(OO)

DATE 15 FEB. 1962

	<u>NO. COPIES</u>		<u>NO. COPIES</u>
Commanding Officer Army Research Office Box CM, Duke Station Durham, North Carolina Attn: Scientific Synthesis Office	(1)	Dr. Albert Lightbody Naval Ordnance Laboratory White Oak, Maryland	(1)
Brookhaven National Laboratory Chemistry Department Upton, New York	(1)	Commanding Officer and Director U. S. Naval Civil Engineering Lab. Port Hueneme, California Attn: Chemistry Division	(1)
Atomic Energy Commission Division of Research Chemistry Programs Washington 25, D. C.	(1)	Dr. A. L. Powell Office of Naval Research Branch Office 495 Summer Street Boston 10, Mass.	(1)
Atomic Energy Commission Division of Technical Information Extension Post Office Box 62 Oak Ridge, Tennessee	(1)	Aeronautical Systems Division ASRCNP Wright-Patterson Air Force Base Ohio	(1)
U.S. Army Chemical Research and Development Laboratories Technical Library Army Chemical Center, Maryland	(1)	Dr. H. C. Clark Department of Chemistry University of British Columbia Vancouver, British Columbia, Canada	(1)
Office of Technical Services Department of Commerce Washington 25, D. C.	(1)	Dr. E. G. Rochow Department of Chemistry Harvard University Cambridge 38, Mass.	(1)
Dr. P. A. Miller Office of Naval Res. Br. Off. 1000 Geary Street San Francisco 9, Calif.	(1)	Dr. John E. Leffler Department of Chemistry Florida State University Tallahassee, Fla.	(1)
Dr. C. Haber Naval Ordnance Laboratory Corona, California	(1)	Dr. William N. Lipscomb Department of Chemistry Harvard University Cambridge, Mass.	(1)
Dr. Porter W. Erickson Chemistry Research Department Non-Metallic Materials Division Naval Ordnance Laboratory White Oak, Maryland	(1)	Dr. T. D. Parsons Department of Chemistry Oregon State College Corvallis, Oregon	(1)

TECHNICAL REPORT DISTRIBUTION LIST

Page 3

CONTRACTOR OLIN MATHIESON CHEMICALS CORPORATION

MR NO. 356-431

CONTRACT NUMBER Nonr 3395(00)

DATE 15 FEB 1962

	<u>NO. COPIES</u>		<u>NO. COPIES</u>
Dr. L. F. Rahn Princeton University Princeton Plastics Laboratory Princeton, New Jersey	(1)	Aircraft Industries Association 7660 Beverly Boulevard Los Angeles 36, Calif. Attn: Mr. H. D. Moran	(10)
Dr. A. V. Tobolsky Department of Chemistry Princeton University Princeton, New Jersey	(1)	American Potash & Chem. Corp. 201 W. Washington Blvd. Whittier, California Attn: Dr. W. S. Emerson	(2)
Dr. R. S. Stein Department of Chemistry University of Massachusetts Amherst, Massachusetts	(1)	U. S. Borax Research Corp. Attn: Dr. Carl Randolph Anaheim, California	(2)
Dr. S. Young Tyree, Jr. Department of Chemistry University of North Carolina Chapel Hill, North Carolina	(1)	General Electric Company Research Laboratory P. O. Box 1088 Schenectady, New York Attn: Dr. J. R. Elliot	(2)
Dr. J. C. Bailar, Jr. Department of Chemistry University of Illinois Urbana, Illinois	(2)	Dr. P. D. George General Electric Company General Engineering Lab. Schenectady, New York	(2)
Dr. L. F. Audrieth Department of Chemistry University of Illinois Urbana, Illinois	(2)	Dr. Hans B. Jonassen Department of Chemistry Tulane University New Orleans 15, Louisiana	(1)
Dr. A. B. Burg Department of Chemistry University of Southern California Los Angeles 7, Calif.	(2)	Dr. Henry Taube Department of Chemistry Stanford University Stanford, Calif.	(1)
Dr. Riley Schaeffer Department of Chemistry Indiana University Bloomington, Indiana	(1)	Plastics Technical Evaluation Center Picatinny Arsenal Dover, N. J.	(1)
Dr. T. G. Fox, Jr., Director of Research Mellon Institute 4400 Fifth Avenue Pittsburgh 13, Pennsylvania	(1)	Dr. G. Barth-Wehrenalp, Director Inorganic Research Department Pennsalt Chemicals Corporation Box 4388 Philadelphia 18, Penna.	(2)

TECHNICAL REPORT DISTRIBUTION LIST

Page 4

CONTRACTOR OLIN MATTHEWSON CHEMICALS CORPORATION

NR NO. 356-431

CONTRACT NUMBER Nonr 3395(00)

DATE 1. FEB 1962

	<u>NO. COPIES</u>		<u>NO. COPIES</u>
Dr. M. M. Chamberlain Department of Chemistry Western Reserve University Cleveland, Ohio	(1)	Dr. D. A. Brown Department of Chemistry University College Upper Merrion Street Dublin, Ireland	(1)
Dr. D. C. Bradley Department of Chemistry University of Western Ontario London, Canada	(1)	Dr. Albert Cotton Department of Chemistry Massachusetts Institute of Technology Cambridge 39, Mass.	(1)
Dr. T. P. Onak Department of Chemistry Los Angeles State College Los Angeles, California	(1)	Dr. Robert R. Holmes Department of Chemistry Carnegie Institute of Technology Pittsburgh 13, Penn.	(1)
Dr. M. J. S. Dewar Department of Chemistry University of Chicago Chicago, Illinois	(1)	Prof. L. A. Bigelow Department of Chemistry Duke University Durham, N. C.	(1)
Dr. M. S. Cohen Thiokol Chemical Corporation Reaction Motors Division Denville, New Jersey	(1)	Dr. William T. Miller Department of Chemistry Cornell University Ithaca, New York	(1)
Inspector of Naval Material 161 Middle Street Bridgeport 3, Conn.	(1)	Prof. Jack Hine Department of Chemistry Georgia Institute of Technology Atlanta 3, Georgia	
Dr. George F. Huff, Vice President Research and Development Callery Chemical Company Callery, Penn.	(1)	Prof. Herbert G. Brown Department of Chemistry Purdue University Lafayette, Indiana	(1)
Dr. Joyce J. Kaufman RIAS 7212 Bollona Avenue Baltimore 12, Maryland	(1)	Dr. Phillip S. Skell Department of Chemistry Pennsylvania State University University Park, Penn.	(1)
Dr. Arthur Finch Royal Holloway College University of London London, England	(1)	Dr. B. D. Post Polytechnic Institute of Brooklyn Brooklyn 1, New York	(1)

TECHNICAL REPORT DISTRIBUTION LIST

Page 5

CONTRACTOR OLIN MATHIESON CHEMICALS CORPORATION

NR NO. 356-431

CONTRACT NUMBER Nonr 3395(00)

DATE 15 FEB. 1962

NO. COPIES

Dr. R. T. Holzmann
Advanced Research Projects Agency
Washington 25, D. C. (1)

Commander
Ordnance Corps
Rock Island Arsenal
Rock Island, Illinois
Attn: ORDBC 9320-ZTO (1)

New York Naval Shipyard
Material Laboratory
Brooklyn 1, New York
Attn: Mr. B. B. Simms (1)

Bureau of Ships,
Department of the Navy
Washington 25, D. C.
Code 660L
Attn: Mr. E. J. Hrycklewicz (1)

Dr. M. F. Hawthorne
Department of Chemistry
University of California, Riverside
Riverside, California (1)

Dr. Roald Hoffman
Department of Chemistry
Harvard University
Cambridge, Massachusetts (1)

Mr. J. A. Kies
Code 6210
Naval Research Laboratory
Washington 25, D. C. (1)

Mr. E. J. Kohn
Code 6110
Naval Research Laboratory
Washington 25, D. C. (1)

Dr. R. B. Fox (1)
Mr. J. E. Cowling (1)
Dr. A. L. Alexander (1)
Dr. D. L. Venezky (1)
Code 6120
Naval Research Laboratory
Washington 25, D. C.

Dr. O. Williams
National Science Foundation
Washington 25, D. C. (1)

Monsanto Research Corporation
1515 Nicholas Road
Dayton, Ohio
Attn: Librarian (1)

Monsanto Research Corporation
Everett Station
Boston 49, Massachusetts
Attn: Librarian

The Dow Chemical Company
ARPA Laboratory
1710 Building
Midland, Michigan (1)

Naval Ordnance Test Station
China Lake, California
Attn: Code 4544 (Dr. Kaufman) (1)
Code 5557 (Mr. S. H. Herzog)
(Mr. R.J. Landry) (1)