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CARBORANE BURNING RATE CATALYSTS

Ross Fitzgerald, et al

Aerojet Solid Propulsion Company

Prepared for:

Air Force Rocket Propulsion Laboratory

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Ross Fitzgerald and Roger B. Steele
Aerojet Solid Propulsion Company

Interim Technical Report
Contract No. F04611-71-C-0066

October 1972

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Air Force Rocket Propulsion Laboratory
Director of Science and Technology
Air Force Systems Command
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13. ABSTRACT

New carborane burning rate catalysts designed for use in solid propellants, without the problems associated with current catalysts, have been prepared. High molecular weight, non-volatile derivatives of bis-(1-carboranylmethyl) ether were synthesized and evaluated for compatibility in HTPB binders as well as compatibility and ballistic properties in aluminized HTPB-UFAP propellants. The alkyl derivative, n-nonyl-bis-(1-carboranylmethyl) ether, has exhibited higher rates in propellant as compared with NHC at the same weight percent but lacks the solubility in HTPB binders required for high catalyst levels. The introduction of unsaturation and branched unsaturation into the side chain of bis-carborane derivatives has provided carboranes which are compatible with HTPB binders at high levels and also exhibit a wide liquid range. Thus, undecylenyl-bis-(1-carboranylmethyl) ether was compatible with cured HTPB at the 50% level after storage for six weeks at 77°F. However, NWC has reported plasticizer bleeding from test propellants containing 5 and 8% of the undecylenyl derivative.

The compound 3,7-dimethyl-2,6-octadienyl-bis-(1-carboranylmethyl) ether has exhibited compatibility with cured HTPB at the 57% level but has not been evaluated in propellant as yet. Both of the unsaturated compounds have remained liquid at -10°C for several weeks. Functionally substituted carboranes, i.e., a diol and a monoisocyanate were also prepared but their utility as burning rate catalysts is limited because of the relatively small amounts of these materials which can be incorporated into the binder polymer chain.

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FOREWORD

This technical report, "Carborane Burning Rate Catalysts", was prepared as partial fulfillment of the requirements of Contract No. F04611-71-C-0066 for the Air Force Rocket Propulsion Laboratory, Director of Science and Technology, Air Force Systems Command, Edwards, California. The work reported was performed in the Propellant Development Department, Advanced Propellants Section of the Aerojet Solid Propulsion Company, Sacramento, California. This report, designated Aerojet Report No. 1840-26SA-1, records the results of work done during the interval 1 July 1971 to 30 September 1972, The program is monitored by Mr. Norman VanderHyde.

Acknowledgement is made to Mr. N. VanderHyde of AFRPL and Mr. J. Braun and F. Pickett of NWC for their aid in selecting promising structures of new carborane burning rate catalysts. Acknowledgement is also made to Mr. R. F. Putnam for the instrumental analyses performed on the new compounds

This technical report has been reviewed and is approved.

CHARLES R. COOKE, Chief
Solid Rocket Division

TABLE OF CONTENTS

TABLE OF CONTENTS

TABLE OF CONTENTS

GLOSSARY

AFRPL	Air Force Rocket Propulsion Laboratory
ASPC	Aerojet Solid Propulsion Company
CMES	Carboranylmethyl ethyl sulfide
DMSO	Dimethylsulfoxide
HMPA	Hexamethylphosphoramide
HTPB	Hydroxy terminated polybutadiene
Hz	Hertz
IPDI	Isophoronediisocyanate
IR, ir	Infrared
I_{sp}	Theoretical specific impulse
m	Multiplet
NHC	n-Hexyl carborane
NMR, nmr	Nuclear magnetic resonance
NWC	Naval Weapons Center
PPM	Parts per million
R-45M	Hydroxy terminated polybutadiene
s	Singlet
t	Triplet
UFAP	Ultrafine ammonium perchlorate

I. INTRODUCTION

This is the first interim technical report submitted in partial fulfillment of the requirements of Contract F04611-71-C-0066. The technical portion of this report covers the period 1 July 1971 to 30 September 1972. Dr. L. J. Rosen is Technical Manager of the program and Drs. R. Fitzgerald and R. B. Steele are the Principal Investigators. A summary of the carboranes prepared during this reporting period is included as Enclosure (1).

II. OBJECTIVE

The objective of the technical effort is to produce carborane burning rate catalysts which can be used in solid propellants without the problems associated with current catalysts such as volatility and hazard sensitivity.

RPL personnel have devised a series of requirements for carborane catalysts which would be acceptable for advanced propellant application.

1. Wide Liquid Range. An ideal compound would have a liquid range of from -65°F to 350°F if used as a plasticizer. Co-cured compounds may have a lesser liquid range.

2. Low Vapor Pressure. The compound must have low volatility at temperatures up to 350°F if used as a plasticizer. Co-cured compounds should have low volatility up to 200°F.

3. High Boron Content. Compounds should have a boron content comparable to or greater than that of NHC to assure a high catalytic effectiveness.

4. Minimal I_{sp} Loss. Compounds should cause little or no loss in I_{sp} when substituted for other binder ingredients in an aluminized composite formulation.

5. Processing Aid. If possible, the compound should act as a processing aid to improve solids loading capability. For this purpose a low viscosity compound is desired.

6. No detrimental Effects on Binder Properties. Mechanical properties of propellant should not be adversely effected by the inclusion of the additives.

7. Non-Migrating. Compounds should be designed so their molecular structure precludes migration. This may be accomplished by bulky molecules or by co-curing with propellant binder.

8. Molecular Structure Flexibility. If possible, the basic molecule should be amenable to addition of various functionalities such as NCO, OH or COOH.

9. Thermal Stability. Compounds should not be subject to thermal degradation or decomposition at temperatures up to 350°F.

10. Chemically Stable. Compounds should not undergo oxidative degradation or chemical interaction with other propellant ingredients at storage or use conditions.

11. Non-Hazardous. Compounds should not be inherently sensitive nor should they sensitize propellants or propellant ingredients.

12. Miscible with Binder. Neat compounds should be miscible with the binder(s) over a wide range of concentrations since the potential requirement for high catalyst levels exists.

13. Efficient Production. The compounds should be amenable to high yield production from safe, simple reactions.

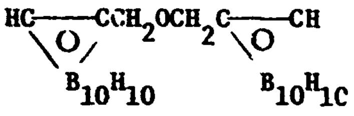
Bis-(1-carboranylmethyl) ether was selected at the inception of the program as the baseline compound for the preparation of new catalysts. Meta-bis-(1-carboranylmethyl) ether and the pentaboranecarborane, 2,4-dicarba-closo-heptaborane, have been selected as new baseline compounds for advanced carborane burning rate catalysts.

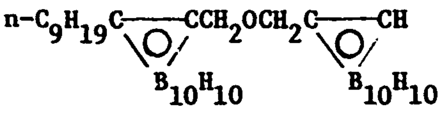
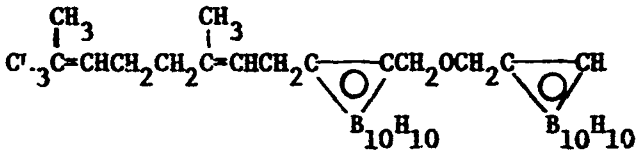
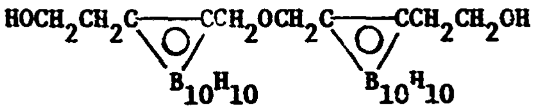
III. SUMMARY

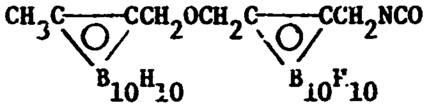
The following is a summary of progress made during the 15 month period 1 July 1971 to 30 September 1972.

A. COMPOUNDS SUBMITTED FOR PROPELLANT EVALUATION

The following compounds were submitted to Naval Weapons Center for propellant evaluation during the current reporting period.

Structure	Quantity Delivered, gm
 $\underset{B_{10}H_{10}}{\underset{\backslash O /}{HC{-}C}}CH_2OCH_2\underset{B_{10}H_{10}}{\underset{\backslash O /}{C{-}CH}}$ Bis-(1-carboranylmethyl) ether m.p. 343-345°C 66% Boron	150

Structure	Quantity Delivered, gm
 $n\text{-}C_9H_{19}\underset{B_{10}H_{10}}{C{-}C}CH_2OCH_2\underset{B_{10}H_{10}}{C{-}CH}$ n-Nonyl-bis-(1-carboranylmethyl) ether m.p. 45-50°C 47% Boron	50
 $CH_2{=}CH(CH_2)_8CH_2\underset{B_{10}H_{10}}{C{-}C}CH_2OCH_2\underset{B_{10}H_{10}}{C{-}CH}$ Undecylenyl-bis-(1-carboranylmethyl) ether m.p. <-10°C 45% Boron	50
 $CH_3\overset{CH_3}{C}{=}CHCH_2CH_2\overset{CH_3}{C}{=}CHCH_2\underset{B_{10}H_{10}}{C{-}C}CH_2OCH_2\underset{B_{10}H_{10}}{C{-}CH}$ 3,7-Dimethyl-2,6-octadienyl-bis(1-carboranylmethyl) ether m.p. <-10°C 46% Boron	50
 $HOCH_2CH_2\underset{B_{10}H_{10}}{C{-}C}CH_2OCH_2\underset{B_{10}H_{10}}{C{-}C}CH_2CH_2OH$ Bis-(2-hydroxyethyl-1-carboranylmethyl) ether m.p. 125-127°C 56% Boron	50

Structure	Quantity Delivered, gm
 2-Methyl-2'-isocyanomethyl-bis-(1-carboranylmethyl) ether m.p. 135.5 - 137.5°C 54% Boron	30

The carboranes evaluated were tested at NWC at the 5 and 8% level in an 86% solids, aluminized HTPB propellant containing 0.5 micron UFAP.

1. n-Nonyl-bis-(1-carboranylmethyl) Ether

The n-nonyl-bis-carborane was found to provide higher burning rates in the test propellant as compared with NHC at the same weight percent. However, plasticizer bleeding was observed from the cured propellant indicating HTPB-plasticizer incompatibility.

2. Undecylenyl-bis-(1-carboranylmethyl) Ether

The undecylenyl-bis-carborane also exuded from the cured propellant when tested at the 5 and 8% level though to a lesser degree than the n-nonyl derivative. However, binder studies have shown the unsaturated bis-carborane to be soluble in liquid and cured HTPB at 150°F at the 60% level. Burning rate data have not yet been obtained with the undecylenyl plasticizer.

3. Bis-(2-β-Hydroxyethyl-1-carboranylmethyl) Ether

The carboranediol was tested only in HTPB binder and was found to be relatively insoluble (about 2%). The material was not evaluated in propellant.

4. 3,7-Dimethyl-2,6-octadienyl-bis-(1-carboranylmethyl) Ether

The dimethyloctadienyl-bis-carborane was found to be most compatible with HTPB. The material is soluble at the 57% level in cured and uncured HTPB at 77°F. Propellant data are not yet available on this plasticizer.

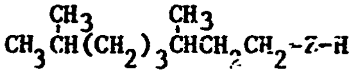
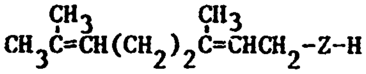
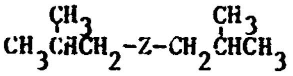
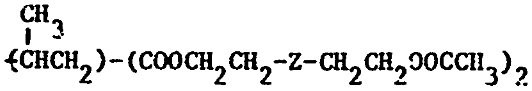
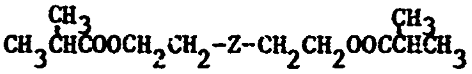
5. Bis-(1-carboranylmethyl) Ether and 2-Methyl-2'-isocyanomethyl-bis-(1-carboranylmethyl) Ether

No propellant or other test data have been made available as yet on the titled solid bis-carborane derivatives.

B. OTHER COMPOUNDS AND INTERMEDIATES

Numerous derivatives of bis-(1-carboranylmethyl) ether were prepared which tentatively do not meet the requirements of wide liquid range or HTPB compatibility. These compounds are listed in Figure 1 along with their melting points and solubilities in cured HTPB binder. Candidate compounds are included for comparison.

MELTING POINTS AND COMPATIBILITY IN HTPB OF DERIVATIVES OF BIS-(1-CARBORANYLMETHYL)ETHER

Compound*	Melting Point, °C	Solubility** in Cured HTPB, %
H-Z-H	343-345	--
CH_3-Z-H	∿280	--
n-C_6H_{13}-Z-H	∿ 50	--
n-C_9H_{19}-Z-H	45-50	∿20
n-$C_{10}H_{21}$-Z-H	23-30	30-40
n-$C_{11}H_{23}$-Z-H	<-10	∿40
n-$C_{12}H_{25}$-Z-H	25-30	>50
n-$C_{13}H_{27}$-Z-H	30-38	>50
n-$C_{14}H_{29}$-Z-H	35-45	<50
 $CH_3\overset{CH_3}{CH}(CH_2)_3\overset{CH_3}{CH}CH_2CH_2\text{-Z-H}$	66-70	<50
$CH_2{=}CH(CH_2)_8CH_2$-Z-H	<-10	>50
 $CH_3\overset{CH_3}{C}{=}CH(CH_2)_2\overset{CH_3}{C}{=}CHCH_2\text{-Z-H}$	<-10	>57
 $CH_3\overset{CH_3}{CH}CH_2\text{-Z-}CH_2\overset{CH_3}{CH}CH_3$	>100	--
$HOCH_2CH_2\text{-Z-}CH_2CH_2OH$	125-127	2.0
 $(\overset{CH_3}{CH}CH_2)\text{-}(COOCH_2CH_2\text{-Z-}CH_2CH_2OOCCH_3)_2$	60	--
$CH_3COOCH_2CH_2\text{-Z-}CH_2CH_2OOCCH_3$	116	--
 $CH_3\overset{CH_3}{CH}COOCH_2CH_2\text{-Z-}CH_2CH_2OOC\overset{CH_3}{CH}CH_3$	104-108	--

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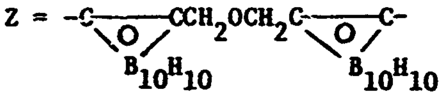
*  $Z = -C\underset{B_{10}H_{10}}{\underset{O}{—}}CCH_2OCH_2C\underset{B_{10}H_{10}}{\underset{O}{—}}C-$

** R-45M/IPDI-Plasticizer cured 72 hours at 140°F

Figure 1
Page 1 of 2

MELTING POINTS AND COMPATIBILITY IN HTPB OF DERIVATIVES OF BIS-(1-CARBORANYLMETHYL) ETHER (cont.)

Compound*	Melting Point, °C	Solubility** in Cured HTPB, %
CH_3-Z-CH_2CH_2OH	188-190	--
CH_3-Z-CH_2COOH	196.5-197.5	--
CH_3-Z-CH_2COCl	129-129.5	--
CH_3-Z-CH_2NCO	135.5-137.5	--

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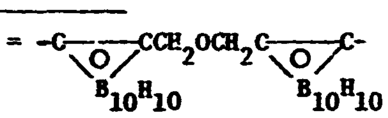
* Z =



$$Z = -C\underset{B_{10}H_{10}}{\backslash O /}CCH_2OCH_2C\underset{B_{10}H_{10}}{\backslash O /}C-$$

Figure 1
Page 2 of 2

IV. TECHNICAL DISCUSSION

A. PREPARATION OF PROPARGYL ETHER

Propargyl ether (I) is the starting material for the preparation of bis-(1-carboranylmethyl) ether and while supplied by the General Analine and Film Corporation during the 1960's, is no longer commercially available. However, a process was developed at ASPC for the production of the acetylenic ether which is simple in design and utilizes commercially available starting materials.* The process consists of treating propargyl alcohol with propargyl bromide in the presence of aqueous sodium hydroxide.

$$HC{\equiv}CCH_2OH + BrCH_2C{\equiv}CH \xrightarrow{NaOH} \underset{I}{HC{\equiv}CCH_2OCH_2C{\equiv}CH} + NaBr$$

The reaction conditions were optimized with respect to alcohol/bromide ratio and reaction time at 77°F. The progress of the reaction was followed by gas liquid phase chromatography. A summary of the experimental results is given in Figure 2. As shown, an alcohol/bromide ratio of 2.8/1 and a twenty-four hour reaction time provide propargyl ether yields on the order of 90%.

B. PREPARATION OF BASELINE CARBORANES

Bis-(1-carboranylmethyl) ether (II) and bis-(2-β-hydroxyethyl-1-carboranylmethyl) ether (III) were selected as the baseline compounds from which the improved carborane burning rate catalysts were prepared. These compounds provided the nuclei for the preparation

---

* This process is based on early research by French workers (Ref. 1).

EFFECT OF ALCOHOL/BROMIDE RATIO AND REACTION TIME ON PROPARGYL ETHER YIELD

$HC\equiv CCH_2OH + HC\equiv CCH_2Br \xrightarrow{NaOH} HC\equiv CCH_2OCH_2\equiv CH$

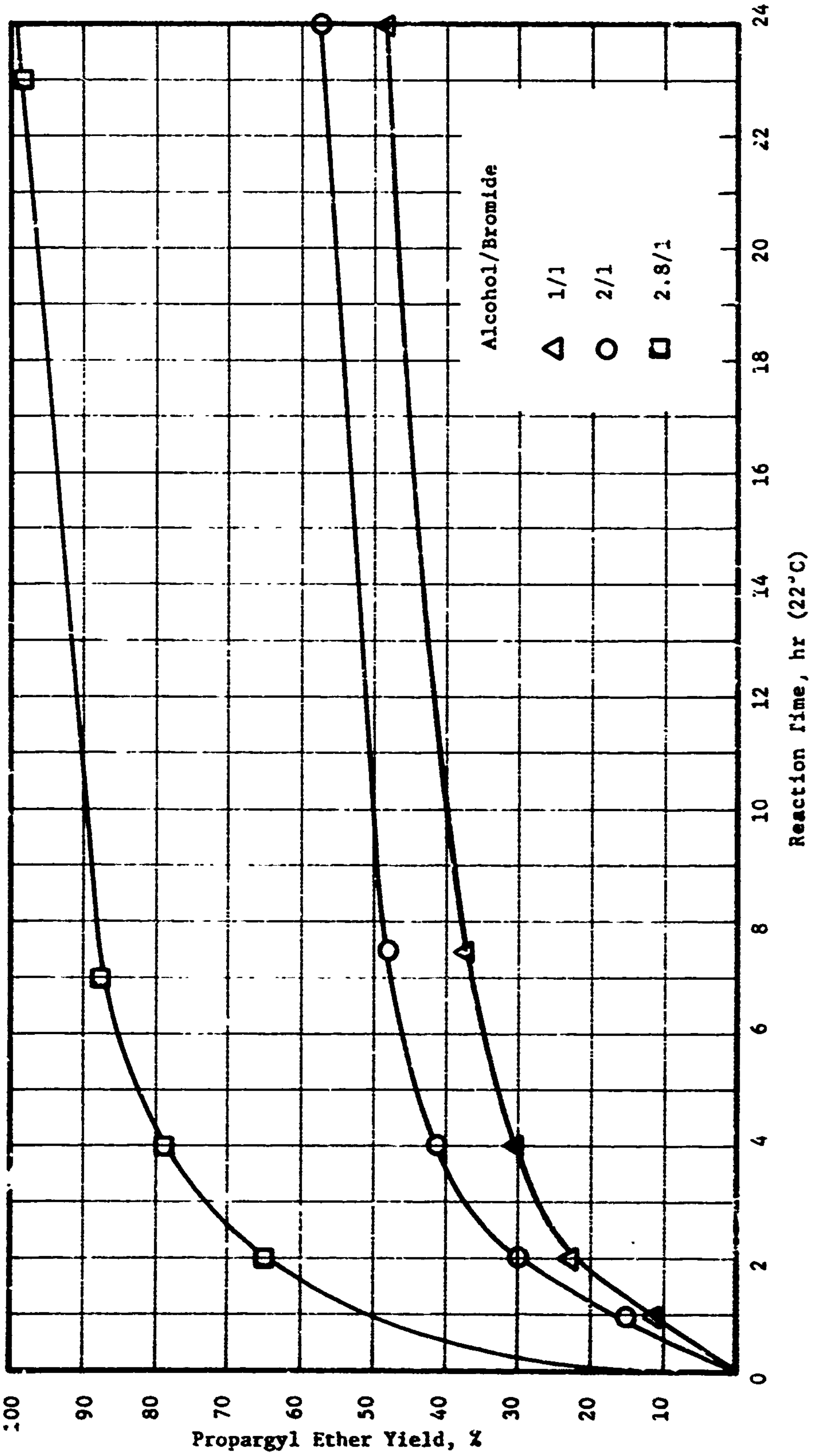


Figure 2

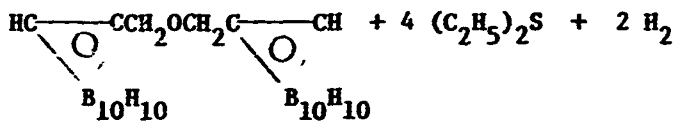
of alkyl-, alkenyl- and ester plasticizers as well as functional carboranes such as alcohols and isocyanates.

1. Bis-(1-carboranylmethyl) Ether (II)

The bis-carborane, II, is the baseline compound from which the burning rate catalysts were prepared. Compound II was synthesized in 50-60% yields via the reaction of 6,9-bis-(diethylsulfide)-decaborane with propargyl ether in dioxane/toluene solvent (Ref. 2). The bis-carborane-dioxane adduct

a. $B_{10}H_{14} + 2\ (C_2H_5)_2S \longrightarrow B_{10}H_{12}\ [(C_2H_5)_2S]_2 + H_2$

b. $2\ B_{10}H_{12}\ [(C_2H_5)S]_2 + HC{\equiv}CCH_2OCH_2C{\equiv}CH \longrightarrow$



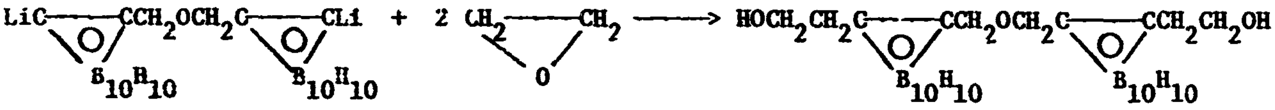
$HC(B_{10}H_{10})CCH_2OCH_2C(B_{10}H_{10})CH + 4\ (C_2H_5)_2S + 2\ H_2$

II

was isolated by filtration and purified by recrystallization from dioxane. The bis-carborane-dioxane adduct was then washed with excess n-hexane to yield pure bis-(1-carboranylmethyl) ether as a white solid melting at 343-345°C. Several pounds of II have been prepared at ASPC by the previously described method. Approximately 150 grams of the bis-carborane have been submitted for propellant evaluation.

2. Bis-(2-β-hydroxyethyl-1-carboranylmethyl) Ether (III)

The carboranediol, III, was utilized as a starting material for a series of potential carboranediester plasticizers. The diol, III, was prepared by treating the dilithium derivative of II with ethylene oxide in ether solvent. After hydrolysis of the reaction mixture the ether solution of the diol was separated and dried. Removal of the ether solvent provided the diol, III, as a white solid melting at 125-127°C in 85% yield. Further purification of the material could be effected by recrystallization from benzene but rigorous drying was required to remove the last traces of benzene from the purified material. Fifty grams of the carborane diol were delivered to NWC.



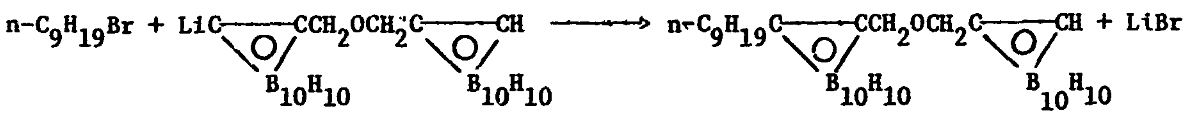
III

C. PREPARATION OF NONFUNCTIONAL CARBORANES (PLASTICIZERS)

1. Alkyl Derivatives

a. n-Nonyl-bis-(1-carboranylmethyl) Ether (IV)

The nonyl derivative IV was the first plasticizer synthesized on this program. The boron content of IV is 47% and comparable to that of n-hexylcarborane (47.5%). It was for this reason that IV was selected for initial evaluation. The plasticizer was prepared via the reaction of n-nonyl bromide with the monolithium derivative of II in ether/dioxane solvent. The plasticizer, IV, was



$$n\text{-}C_9H_{19}Br + Li\underset{\substack{\backslash O/\\ B_{10}H_{10}}}{C\text{---}C}CH_2OCH_2\underset{\substack{\backslash O/\\ B_{10}H_{10}}}{C\text{---}C}H \longrightarrow n\text{-}C_9H_{19}\underset{\substack{\backslash O/\\ B_{10}H_{10}}}{C\text{---}C}CH_2OCH_2\underset{\substack{\backslash O/\\ B_{10}H_{10}}}{C\text{---}C}H + LiBr$$

IV

separated from unreacted II by treatment with n-hexane followed by filtration. After removal of excess n-nonyl bromide under high vacuum, the residue was purified by column chromatography (n-hexane solution of IV on silica gel) to yield IV as a colorless liquid. The compound remained liquid for several weeks at -10°C but a sample stored at laboratory temperatures at NWC solidified. Later, the material also crystallized at ASPC.

The experimental conditions were optimized with respect to reaction temperature for 24 hour reaction time. The data, summarized in Figure 3, show that elevating the reaction temperature to 90°C provided the best yields of alkylcarborane IV.

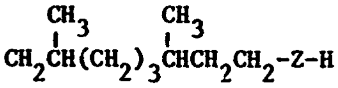
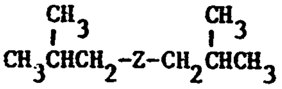
Several alkyl-bis-(1-carboranylmethyl) ethers were prepared by the previously described method. These compounds are listed in Figure 4 along with their yields and melting points. The data show that a melting point minimum appears to occur at the undecyl-bis-carborane (C_{11}). Interestingly, the symmetrical diisobutyl-bis-carbornae melted above 100°C while the n-octyl derivative containing the same total number of substituent carbon atoms exhibited a melting point of about 50°C. These data emphasize the importance of molecular symmetry with respect to liquid range, i.e., symmetrical molecules must be avoided in order to produce

EFFECT OF REACTION TEMPERATURE ON THE YIELD OF n-NONYL-BIS-(1-CARBORANYLMETHYL) ETHER (IV)

Reaction Temperature, °C	Yield of IV, %
18 hours at 40°	25
16 hours at 40°, 2 hours at 90°	50
14 hours at 40°, 4 hours at 90°	55

Figure 3

MELTING POINTS OF ALKYL DERIVATIVES OF BIS-(1-CARBORANYLMETHYL) ETHER

Compound*	Melting Point, °C	Yield, %
H-Z-H	343-345	59
CH_3-Z-H	∿280	40
n-C_6H_{13}-Z-H	∿50	45
n-C_8H_{17}-Z-H	∿50	40
n-C_9H_{19}-Z-H	45-50	50
n-$C_{10}H_{21}$-Z-H	23-30	45
n-$C_{11}H_{23}$-Z-H	<-10	40
n-$C_{12}H_{25}$-Z-H	25-30	38
n-$C_{13}H_{27}$-Z-H	30-38	30
n-$C_{14}H_{29}$-Z-H	35-45	25
 $CH_2\overset{CH_3}{CH}(CH_2)_3\overset{CH_3}{CH}CH_2CH_2\text{-Z-H}$	66-70	35
 $CH_3\overset{CH_3}{CH}CH_2\text{-Z-}CH_2\overset{CH_3}{CH}CH_3$	>100	90

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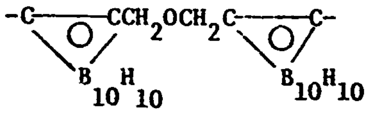
* Z = 

Figure 4

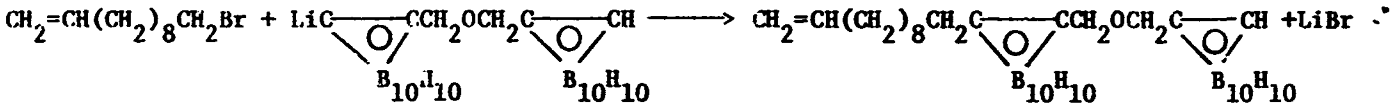
bis-carborane derivatives with low-melting points.

2 Alkenyl Derivatives

Alkenyl, or unsaturated, substituents, are most effective to date at reducing the melting point of bis-(1-carboranylmethyl) ether derivatives. Substituents containing branching as well as unsaturation are particularly effective at increasing liquid range and HTPB compatibility of bis-carboranes.

a. Undecylenyl-bis-(1-carboranylmethyl) Ether (V)

The unsaturated bis-carborane V was prepared from undecylenyl bromide and the monolithium derivative of II in ether solvent



V

After removal of unreacted bromide under high vacuum, the unsaturated derivate V was purified by column chromatography (n-hexane solution on silica gel) to yield a clear liquid melting below -10°C and boiling above 250°C (0.1mm).

Considerable effort was expended in optimizing the experimental conditions required to produce the best yields of V. Various reaction conditions and their effect on the yield of V are summarized in Figure 5. The data show that a long reaction time in

EFFECT OF REACTION CONDITIONS ON YIELD OF UNDECYLENYL-BIS-(1-CARBORANYLMETHYL) ETHER

Carborane/Halide	Solvent	Base	Rxn Time	Rxn Temp, °C	% Yield
2/1	$\mathrm{Et_2O}$/Dioxane	BuLi	20 hr	60° 18 hr 90° 1 hr	10
1/1	$\mathrm{Et_2O}$/Dioxane	BuLi	4 days	50° 2 hr 95° 4 days	10
1/1	Dioxane	NaH	20 hrs	100°	5
1/3	Dioxane	BuLi	3 days	100°	15
1/3	$\mathrm{Et_2O}$/Dioxane	BuLi	16 hrs	60°	20
1/3	$\mathrm{Et_2O}$/DMSO*	BuLi	16 hrs	70°	25
1/2	$\mathrm{Et_2O}$/Dioxane/DMSO	BuLi	16 hrs	50°	10
1/3	$\mathrm{Et_2O}$/HMPA**	BuLi	16 hrs	60°	15
1/3	$\mathrm{Et_2O}$	BuLi	72 hrs	38°	44

---

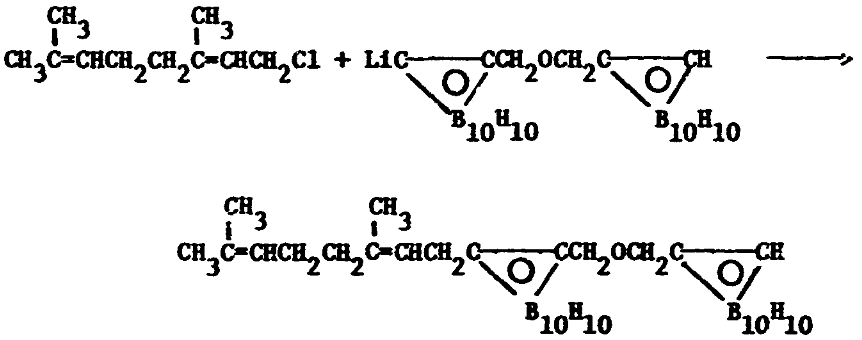
* Dimethylsulfoxide
** Hexamethylphosphoramide

Figure 5

ether solvent at low temperature provides the highest yield of undecylenyl-bis-(1-carboranylmethyl) ether, V.

b. 3,7-Dimethyl-2,6-octadienyl-bis-(1-carboranylmethyl) ether VI

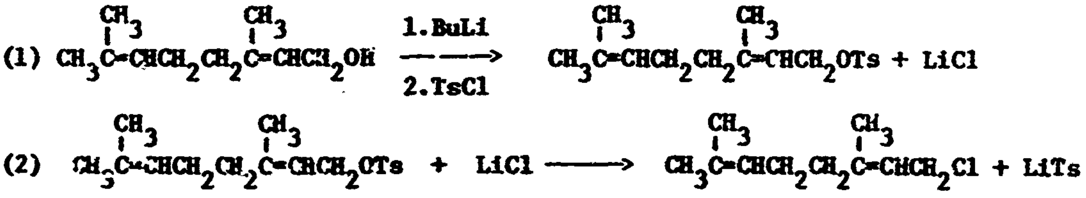
The derivative, VI, was prepared in the usual manner from geranyl chloride and the monolithium derivative of II.



VI

After purification by column chromatography VI was obtained as a clear liquid melting below -10°C and boiling above 150°C (0.1mm).

The geranyl chloride starting material is not commercially available but was obtained in our laboratory via the reaction of lithium chloride with geranyl tosylate. The tosylate was derived from the lithium derivative of geraniol and p-toluenesulfonyl chloride.



$$(1)\quad \mathrm{CH_3\overset{CH_3}{\overset{|}{C}}{=}CHCH_2CH_2\overset{CH_3}{\overset{|}{C}}{=}CHCH_2OH} \xrightarrow[\text{2.TsCl}]{\text{1.BuLi}} \mathrm{CH_3\overset{CH_3}{\overset{|}{C}}{=}CHCH_2CH_2\overset{CH_3}{\overset{|}{C}}{=}CHCH_2OTs + LiCl}$$

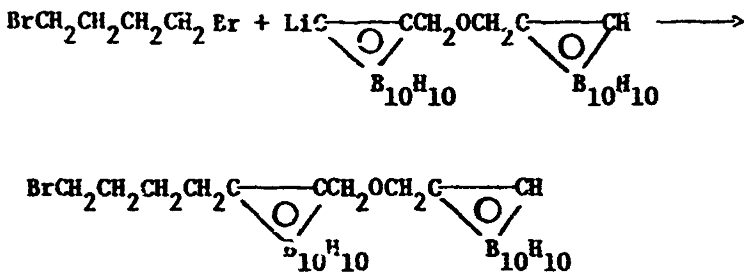
$$(2)\quad \mathrm{CH_3\overset{CH_3}{\overset{|}{C}}{=}CHCH_2CH_2\overset{CH_3}{\overset{|}{C}}{=}CHCH_2OTs + LiCl} \longrightarrow \mathrm{CH_3\overset{CH_3}{\overset{|}{C}}{=}CHCH_2CH_2\overset{CH_3}{\overset{|}{C}}{=}CHCH_2Cl + LiTs}$$

The geranyl chloride is obtained in approximately 60% overall yield as a clear liquid boiling at 65°C (0.5mm).

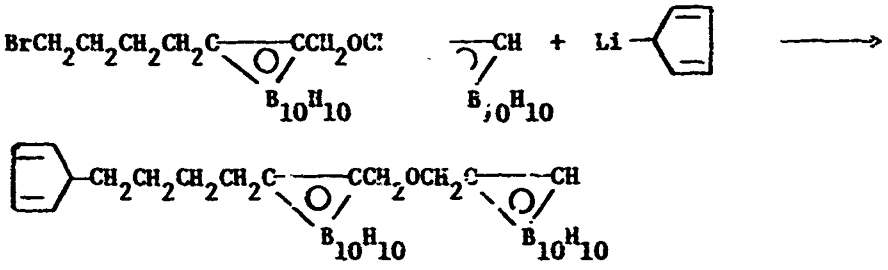
c. 4-Cyclopentadienyl-n-butyl-bis-(1-carboranylmethyl) Ether (VII)

The cyclopentadenyl derivative VII is expected to exhibit substantial resistance to migration in HTPB propellants (a) by bonding to HTPB double bonds during a high temperature post cure period, or (b) due to the enhanced association of the cyclopentadienyl moiety with the HTPB unsaturated structure. The synthesis of VII consists of first preparing 4-bromo-n-butyl-bis-(1-carboranylmethyl) ether and then treating this material with the lithium derivative of cyclopentadiene

(1)



(2)



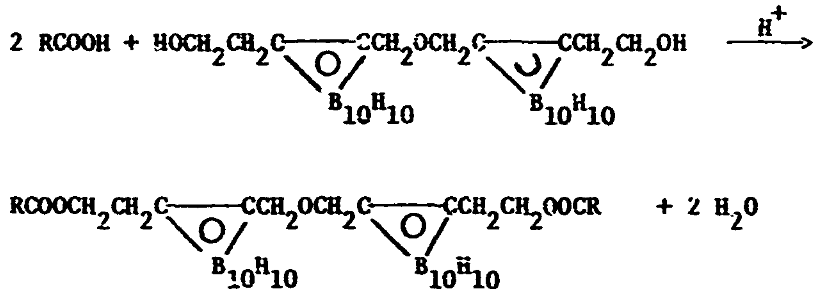
VII

The reaction sequence has been completed to the bromobutyl-bis-carborane, reaction (1).

3. Ester Plasticizers

Several ester derivatives were prepared from the carborane baseline diol III in anticipation of providing liquid carborane ester plasticizers. However, all of the carborane esters prepared were relatively high melting solids.

The general procedure for preparing the carborane esters was to treat monofunctional acids with the baseline carboranediol III in the presence of an acid catalyst.



$$2\,RCOOH + HOCH_2CH_2\underset{B_{10}H_{10}}{\underbrace{C\overset{O}{—}C}}CH_2OCH_2\underset{B_{10}H_{10}}{\underbrace{C\overset{O}{—}C}}CH_2CH_2OH \xrightarrow{H^+}$$

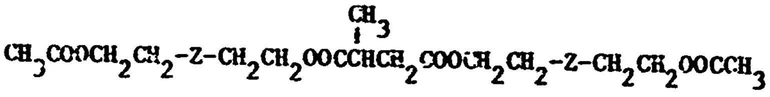
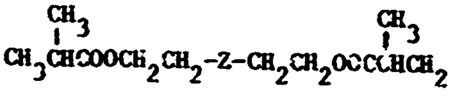
$$RCOOCH_2CH_2\underset{B_{10}H_{10}}{\underbrace{C\overset{O}{—}C}}CH_2OCH_2\underset{B_{10}H_{10}}{\underbrace{C\overset{O}{—}C}}CH_2CH_2OOCR + 2\,H_2O$$

The carborane esters prepared in this manner, as well as their melting points and yields, are listed in Figure 6. As shown, the ester derivatives all exhibited melting points too high for effective plasticizers.

D. PREPARATION OF MONOFUNCTIONAL CARBORANES

Several monofunctional derivatives of bis-(1-carboranylmethyl) ether were prepared during the current reporting period. These compounds were all intermediates leading to the synthesis of a carborane isocyanate.

CARBORANE ESTER PLASTICIZERS*

Compound	Melting Point, °C	Yield, %
 $CH_3COOCH_2CH_2\text{-Z-}CH_2CH_2OOC\overset{CH_3}{C}HCH_2COOCH_2CH_2\text{-Z-}CH_2CH_2OOCCH_3$	60	80
$CH_3COOCH_2CH_2\text{-Z-}CH_2CH_2OOCCH_3$	116	85
 $CH_3\overset{CH_3}{C}HCOOCH_2CH_2\text{-Z-}CH_2CH_2OOC\overset{CH_3}{C}HCH_2$	104-108	87

* Z =

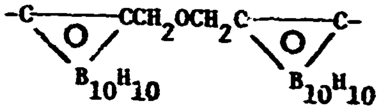
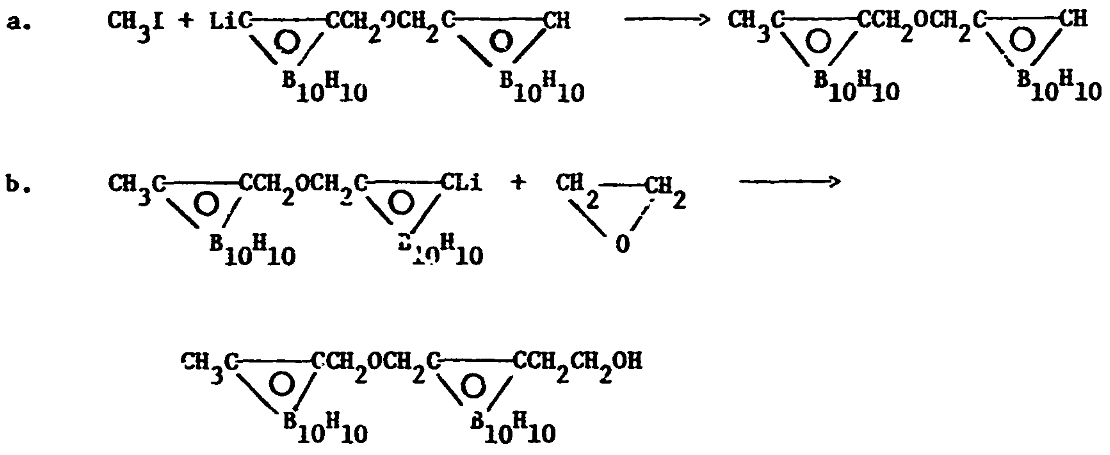


Figure 6

1. 2-Methyl-2'-hydroxyethyl-bis-(1-carboranylmethyl) Ether (VIII)

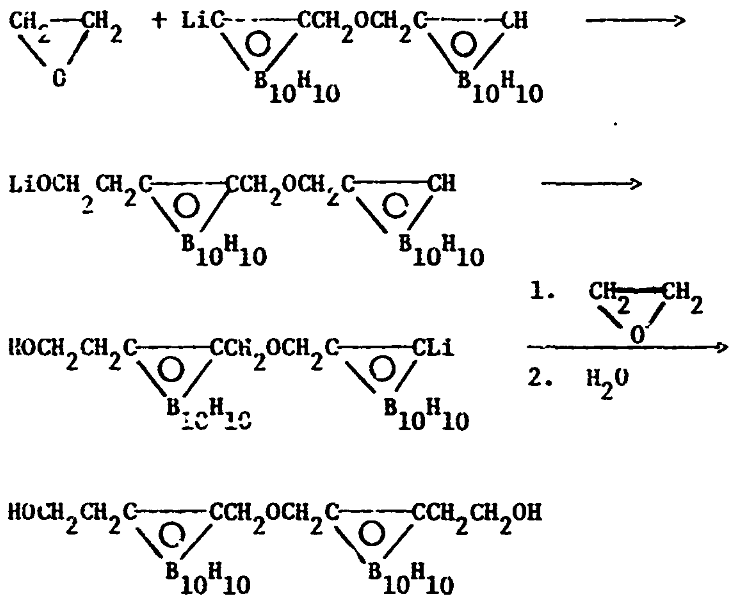
Methyl-bis-carborane was prepared from methyl iodide and the monolithium derivative of II. The monofunctional alcohol VIII was in turn prepared by treating lithio methyl-bis-carborane with ethylene oxide.



VIII

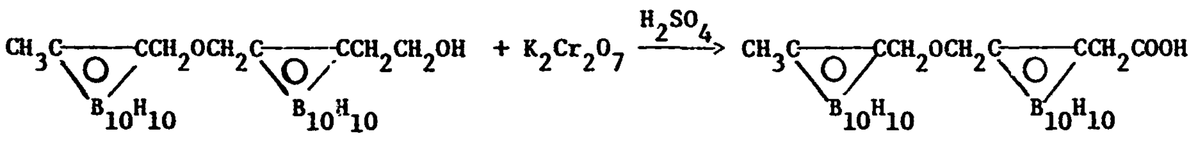
The alcohol VIII was obtained in approximatey 40% yield as a white solid melting at 188-190°C.

The methyl derivative of II was selected for hydroxylation since treatment of the monolithium derivative of unsubstituted II with ethylene oxide resulted in the formation of the diol, bis-(2-β-hydroxyethyl-1-carboranylmethyl) ether, and unreacted II. Apparently the intermediate lithium derivative of the desired monofunctional alcohol rearranges to an intermediate which, in turn, reacts with a second molecule of ethylene oxide.



2. 2-Methyl-2'-carboxymethyl-bis-(1-carboranylmethyl) Ether (IX)

The carborane carboxylic acid IX was obtained by chromic acid oxidation of the previously described alcohol VIII.

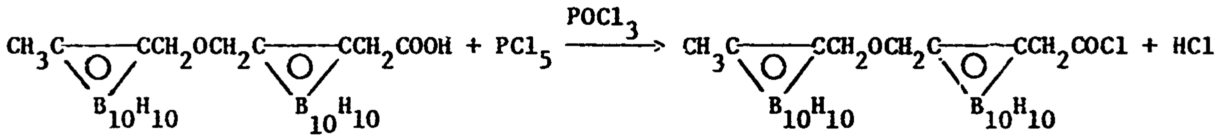


IX

The carboxylic acid IX was purified by crystallization from chloroform to give a 75% yield of material melting at 196.5 - 197.5°C.

3. 2-Methyl-2'-acetylchloro-bis-(1-carboranylmethyl) Ether (X)

The acid chloride X was obtained by treating the carboranecarboxylic acid, IX, with PCl_5 in $POCl_3$ solvent.

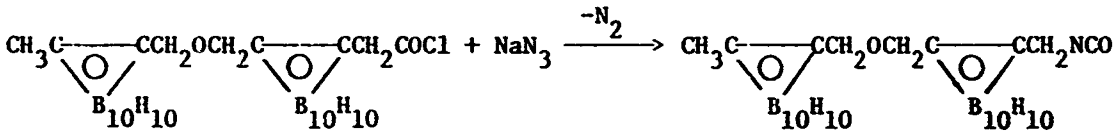


X

Removal of the solvent provided the desired carborane acid chloride X in 80% yield. Crystallization from pentane gave pure X melting at 129-129.5.

4. 2-Methyl-2'-isocyano-bis-(1-carboranylmethyl) Ether (XI)

The carboranylisocyanate, XI, was prepared from the acid chloride X by treatment with sodium azide. The carboranylisocyanate, XI, was



XI

obtained as a white solid melting at 135.5 - 137.5°C.

E. META-BIS-(1-CARBORANYLMETHYL) ETHERS

It has been demonstrated that meta-carborane produces lower melting derivatives as compared with ortho-carborane (Reference 3). On this basis derivatives of meta-bis-(1-carboranylmethyl) ether, XII, should provide a series of carborane catalysts with wide liquid range. For this reason the thermal isomerization of II to the corresponding meta-derivative was attempted. Samples of II were

$$\text{II} \xrightarrow{\Delta} HCB_{10}H_{10}CCH_2OCH_2CB_{10}H_{10}CH \; *$$

XII

held at 370 and 400°C for 18 hours. Methyl-meta-carborane was tentatively identified in the product indicating that the bis-carboranyl ether, II, had been cleaved during the thermal process. Experiments are now in progress to determine the optimum isomerization temperature.

The meta compound, XII, will be synthesized from the monolithium derivative of meta-carborane and bis-chloromethyl ether in order to provide pure material for comparison with isomerization products.

$$2\ HCB_{10}H_{10}CLi \;+\; ClCH_2OCH_2Cl \longrightarrow HCB_{10}H_{10}CCH_2OCH_2CB_{10}H_{10}CH$$

XII

Derivatives of XII should be low melting and thus provide the wide liquid range desired for the new catalysts.

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* Meta-carborane is designated as $HCB_{10}H_{10}CH$ as opposed to  $HC\overset{\backslash O /}{—}CH$, $B_{10}H_{10}$ for ortho-carborane.

F. PENTABORANECARBORANES

Attempts were made to prepare carboranes based on pentaborane. Significant cost savings could be realized from the production of B_5 carboranes as burning rate catalysts because of the availability and relatively low cost of pentaborane as compared with decaborane.

Initial attempts at processing pentaborane were unsuccessful because of the toxicity and pyrophoric nature of this material. More recently the desired starting material for pentaboranecarboranes, 2,4-dicarba-closo-heptaborane ($C_2B_5H_7$), was purchased from Chemical Systems, Inc. The availability of the B_5 carborane will enormously accelerate the production of useful burning rate catalysts based on pentaborane. Pentaborane carboranes tentatively selected for synthesis are shown below.

PENTABORANECARBORANES

$H(C_2B_5H_5)CH_2OCH_2(C_2B_5H_5)H$

51% Boron

$CH_3(C_2B_5H_5)CH_2OCH_2(C_2B_5H_5)CH_3$

45% Boron

G. COMPATIBILITY STUDIES

The compatibility of bis-carborane plasticizers was determined in HTPB binders and propellants. Binder compatibility studies were performed at ASPC and propellant evaluations were conducted at the Naval Weapons Center, China Lake, California.

1. Compatibility in HTPB Binders

The compatibility of bis-carborane plasticizers in cured R-45M was determined by mixing specified amounts of plasticizer with a stoichiometric blend of R-45M and IPDI.* The samples, 2 gram, were degassed for 20 minutes at 77°F, warmed to approximately 150°F in order to obtain a clear solution and then cured for 72 hours at 140°F. It should be noted here that all plasticizers tested at the 50% level, except the dimethyloctadienyl derivative, VI, produced turbid binder samples at room temperature. However, heating to 150°F provided clear, homogeneous solutions in all cases tested. The dimethyloctadienyl derivative, on the other hand, afforded clear liquid binder samples at room temperature when mixed with HTPB/IPDI at the 57% level.

a. Alkyl-bis-carboranes

The compatibility data, summarized in Figure 7, show that the solubility of alkyl-bis-carboranes in cured HTPB increases as the number of substituent carbon atoms is increased up to C_{13}. Interestingly, the C_{14} derivative afforded a cloudy cured binder sample indicating incompatibility of this material at the 50% level.

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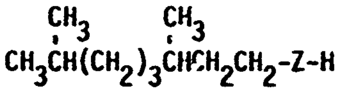
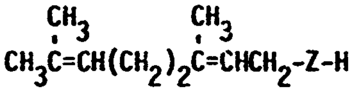
* Isophoronediisocyanate

COMPATIBILITY OF Bis-CARBORANE DERIVATIVES IN CURED HTPB*

Compound **	Solubility in R-45M, %
$n\text{-}C_9H_{19}\text{-}Z\text{-}H$	∿ 20
$n\text{-}C_{10}H_{21}\text{-}Z\text{-}H$	30-40
$n\text{-}C_{11}H_{23}\text{-}Z\text{-}H$	∿ 40
$n\text{-}C_{12}H_{25}\text{-}Z\text{-}H$	> 50
$n\text{-}C_{13}H_{27}\text{-}Z\text{-}H$	> 50
$n\text{-}C_{14}H_{29}\text{-}Z\text{-}H$	< 50
 $CH_3\overset{CH_3}{C}H(CH_2)_3\overset{CH_3}{C}HCH_2CH_2\text{-}Z\text{-}H$	< 50
$CH_2{=}CH(CH_2)_8CH_2\text{-}Z\text{-}H$	> 60
 $CH_3\overset{CH_3}{C}{=}CH(CH_2)_2\overset{CH_3}{C}{=}CHCH_2\text{-}Z\text{-}H$	> 57
$HOCH_2CH_2\text{-}Z\text{-}CH_2CH_2OH$	2.0

---

* Equivalent amounts of R-45M and IPDI/Plasticizer cured 72 hours at 140°F.

** Z =

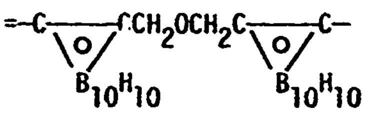


Figure 7

The branched dimethyloctyl derivative appeared superior to the n-decyl derivative although neither material afforded clear, cured binder samples.

b. Alkenyl-bis-carboranes

The introduction of unsaturation into the substituent side chains provided bis-carboranes with significantly improved compatibility in HTPB binders as compared with alkyl derivatives. As shown in Figure 7, the undecylenyl and dimethyloctadienyl derivatives provided clear, cured HTPB binders containing 60 and 57% plasticizer, respectively. In contrast to these results, the saturated analogs, i.e., the undecyl and dimethyloctyl derivatives were both incompatible in cured HTPB at the 50% level.

It is important to note that the undecylenyl-bis-carborane, V, at the 50 and 60% level, formed a turbid mixture with R-45M/IPDI at 77°F which cleared at 140-150°F. The cured samples, however, remained clear and no plasticizer exudation was observed at 150°F or on cooling to 77°F.

On the other hand, the dimethyloctadienyl-bis-carborane, VI, at the 57% level formed a clear solution with R-45M/IPDI at 77°F. The cured sample remained clear with no evidence of plasticizer exudation.

c. Bis-(2-β-Hydroxyethyl-1-carboranylmethyl) Ether

The carborane diol, III, was tested by NWC and found to be 2% soluble in R-45M. No further work was done with this compound.

2. Compatibility in HTPB Propellants

The n-nonyl- and undecylenyl-bis-carboranes were evaluated at NWC for compatibility at the 5 and 8% level in an 86% solids aluminized propellant containing A-4 coated 0.5 micron UFAP. The propellants containing the experimental plasticizers were mixed, cast and cured for seven days at 140°F. At the end of the cure cycle both the n-nonyl- and undecylenyl-bis-carborane plasticized propellants (5 and 8%) exhibited plasticizer bleeding. The dimethyloctadienyl derivative has not yet been evaluated in the test propellants.

It is of interest that the n-nonyl-bis-carborane was reported to provide higher burning rates in the test propellants as compared with NHC at the same weight percent.

V. EXPERIMENTAL SECTION

A. DIPROPARGYL ETHER I

To a 5 l round bottom flask containing 1.5 l of aqueous 0.8 N sodium hydroxide solution was added dropwise a mixture of propargyl bromide, 720g (6.0 mole) and propargyl alcohol, 940g (16.8 mole). During this addition, the temperature of the reaction mixture was kept between 25 and 30°C through cooling with an ice-water bath. The two phase reaction mixture was then stirred vigorously (magnetic stirring bar) for 24 hours. This transformation, involves formation of a product which is immiscible with, and less dense than water, from reactants which are partially soluable in, and whose combined densities are greater than that of water. Consequently, the initial lower organic layer rises to the top as the reaction proceeds.

On completion of the reaction the upper organic layer was separated, washed successively with 2% sodium chloride solution (3 x 500 ml), 5% sodium bicarbonate solution (1 x 500 ml), 4% sodium chloride solution (1 x 500 ml) and dried ($MgSO_4$). The dry dipropargyl ether was distilled at atmospheric pressure yielding 490g (82%) of light yellow product: Bp 122-123°C/760 mm (reported bp 119-120°C Ref. 1).

B. BIS-(1-CARBORANYLMETHYL) ETHER II

Into a 5 l, three-neck flask, under a positive nitrogen atmosphere, was added 500 g (4.1 mole) of decaborane, followed by 500 ml of ethyl sulfide, 250 ml of dry toluene and 250 ml of dry dioxane. This solution was stirred (air driven mechanical stirrer) at ambient temperature for 24 hours while hydrogen was evolved and bis-(diethyl sulfide)-decaborane was formed. The reaction mixture was then heated to 70°C and 193 g (2.05 mole) of dipropargyl was added at a rate necessary to maintain a controllable reflux. During the addition, which required approximately 6 hours, V.B (cont.)

hydrogen is evolved rapidly. After the addition was complete, the reaction mixture was heated at strong reflux for 1 hour than stirred overnight without further heating. On cooling to -50°C (dry ice/methanol), a copious precipitate, bis-(1-carboranylmethyl) ether, formed. The product was separated by filtration and recrystallized from dioxane. This crop of crystals, reported to be the monodioxanate (Ref. 2), was recrystallized again from dioxane, washed with hexane (4 x 500 ml) and dried in a vacuum oven (50°C) for 18 hours yielding 400 g (59%) of white crystaline bis-(1-carboranylmethyl) ether: mp 342-344°C (reported mp 342-34[illegible].5 °C Ref. 2); ir(KBr) 2595 (B-H), 3350 (C-H) and 1132 cm^{-1} (CH_2-O); nmr(acetone $\underline{d}_6$), δ 3.92 (s, 4, $C\underline{H}_2$), and 4.47 ppm (s(broad), 2, C-$\underline{H}$).

C. BIS-(2-β-HYDROXYETHYL-1-CARBORANYLMETHYL) ETHER III

Bis-(1-carboranylmethyl) ether, 25 g (0.075 mole) in 200 ml of anhydrous ethyl ether was treated at 0°C with a hexane solution of butyl lithium (0.15 mole butyl lithium) under a dry nitrogen atmosphere. To the resulting di-lithio-bis-(1-carboranylmethyl) ether was added 8.8 g (0.20 mole) of ethylene oxide as a solution in 100 ml of diethyl ether. The reaction mixture was allowed to stir for 30 minutes, then treated with a 10% hydrochloric acid-ice water solution. The resulting two phase system was separated and the organic layer washed with saturated sodium chloride solution (2 x 150 ml) and dried ($MgSO_4$). On concentration to dryness a white powder was obtained which on recrystallization from benzene gave 36 g (85%) of bis-(2-β-hydroxyethyl-1-carboranylmethyl) ether: mp 125-127°C (reported mp 126-128 °C Ref. 2); nmr (acetone $\underline{d}_6$) δ 2.48 (t, 4, J = 7Hz, C-$C\underline{H}_2$), 2.97 (s(broad). 2, O-$\underline{H}$), 3.[illegible]0 (t, 4, J = 7Hz, $C\underline{H}_2$-OH), and 4.26 ppm (s, 4, $C\underline{H}_2$-O-$C\underline{H}_2$).

D. ALKYL-BIS-(1-CARBORANYLMETHYL) ETHER

The following is a representative procedure for the synthesis of a series of alkenyl and alkyl substituted carboranes. A solution of

V.D (cont.)

5.0g (0.015 mole) of bis-(1-carboranylmethyl) ether in 60 ml of anhydrous diethyl ether, under a nitrogen atmosphere, was cooled (ice-water bath) then treated with butyl lithium (0.016 mole as a 15% solution in hexane) while maintaining a temperature of between 10 and 20°C. The ethereal solution was then allowed to equilibrate to ambient temperature and 10.6 g (0.046 mole) of undecylenyl bromide was added by syringe. The reaction mixture was then boiled at gentle reflux (~38°C) for 72 hours. On cooling, 50 ml of 5% hydrochloric acid was added and the organic layer from the resulting two phase mixture was separated, washed with saturated sodium chloride solution (3 x 100 ml) and dried ($MgSO_4$). This mixture was concentrated by distillation at reduced pressure to a brownish oily residue. The residue was dissolved in a minimum amount of hexane and eluted through a silica gel column (25 x 600 mm) with hexane solvent. Concentration of the eluent yielded 3.1g (43%) of clear liquid undecylenyl-bis-1-carboranylmethyl) ether V: mp <-10°C, bp >250°C/1 mm, ir(neat) 3060 (C-H on carborane), 2850 and 2930 (CH_2), 1640 (C=C) and 1140 cm^{-1} (C-O); nmr δ 1.0 to 2.2 (m(broad), 18,($CH_2)_9$), 3.78 (s, 2, CH_2-O), 3.81 (s, 2, CH_2-O) and 5.0 to 5.28 ppm (m, 3, vinyl).

<u>Anal</u>. Calcd for $C_{17}H_{46}B_{20}O$: B, 44.8. Found: B, 43.7

The previously described procedure was employed for the preparation of several alkyl-bis-carboranes. These compounds are listed in Figure 4 along with their yields and melting points. The NMR and IR spectra of these compounds were consistent with their proposed structures.

E. 1-CHLORO-3,7-DIMETHYL-2,6-OCTADIENE

A solution of 30.8g (0.20 mole) of 3,7-dimethyl-2,6-octadien-1-ol in 90 ml of diethyl ether and 45 ml of hexamethylphosphoramide was treated at room temperature with one equivalent of butyl lithium (as a 15% solution in

V.E (cont.)

hexane). To the resulting mixture was added 40g (0.21 mole) of p-toluenesulfonyl chloride followed by a solution of lithium chloride, 24g (0.57 mole), in 100 ml of a 2:1 mixture of diethyl ether: hexamethylphosphoramide. To this solution, after standing overnight, was added 200 ml of water and the resulting two phase mixture separated. The organic layer was washed with saturated sodium chloride solution (4 x 100 ml), dried ($MgSO_4$) and concentrated to a dark liquid residue by rotary evaporation. The residue, on distillation at reduced pressure, gave 20g (58%) of 1-chloro-3,7-dimethyl-2,6-octadiene: bp 63-66°C/0.5 mm (reported bp 64-65°C/0.05 mm, Ref. 4).

F. 3,7-DIMETHYL-2,6-OCTADIENYL-BIS-(1-CARBORANYLMETHYL) ETHER VI

To a cooled (ice-water bath) solution of 5.0g (0.015 mole) of bis-(1-carboranylmethyl) ether in 50 ml of anhydrous diethyl ether was added one equivalent of butyl lithium (as a 15% solution in hexane). After warming to room temperature, the resulting solution was treated with 5.0 g (0.028 mole) of 1-chloro-3,7-dimethyl-2,6-octadiene and allowed to stand overnight at room temperature. At this time, 50 ml of 5% hydrochloric acid was added to the reaction mixture and the resulting two phase mixture separated. The ethereal phase was washed with saturated sodium chloride solution (3 x 50 ml), dried ($MgSO_4$) and concentrated by distillation at reduced pressure. The residue was dissolved in a minimum amount of hexane and eluted through a silica gel column. Concentration of the combined eluents, by rotary evaporation, afforded 3.7g (52%) of 3,7-dimethyl-2,6-octadienyl-bis-(1-carboranylmethyl) ether: mp <-10°C ; ir 3080 (C-H carborane), 2930 (CH_2), 2600 (BH), 1665, 1675 (C=C) and 1140 cm^{-1} (C-O); nmr δ 1.0 to 2.95 (m(broad), 6, $C\underline{H}_2$), 1.55 (s, 6, $=C\begin{smallmatrix} \diagup C\underline{H}_3 \\ \diagdown C\underline{H}_3 \end{smallmatrix}$), 1.68 (s, 3, $=C\diagup^{C\underline{H}_3}$), 3.84 and 3.86 (s overlaping $C\underline{H}_2$-O-$C\underline{H}_2$) and 4.5 to 5.25 ppm (m, 2, vinyl).

V. (cont.)

G. BIS-(ISOBUTYLCARBORANYLMETHYL) ETHER

A solution of 3.3g (0.01 mole) bis-(1-carboranylmethyl) ether in 25 ml of anhydrous ethyl ether, held between 5 and 10°C, was treated with two equivalents of butyl lithium (as a 15% solution in hexane). After stirring for 0.5 hour, isobutyl bromide, 6.8g (0.05 mole) was added to the reaction mixture and the solution was heated to 50°C for 18 hours. The reaction mixture was then diluted with 25 ml of water and the phases separated. The organic layer was washed with saturated sodium-chloride solution (3 x 25 ml), dried ($MgSO_4$) and concentrated by distillation at reduced pressure to white crystalline bis-(isobutylcarboranylmethyl) ether: mp >100°C; the ir spectrum was consistent with the assigned structure.

H. DIACETATE ESTER OF BIS-2-β-HYDROXYETHYL-1-CARBORANYLMETHYL) ETHER

To 5 ml of acetic anhydride was added 1.0g (2.4 mole) of bis-2-β-hydroxyethyl-1-carboranylmethyl) ether. The reaction mixture was boiled at reflux for 24 hours then stripped of solvent by distillation at reduced pressure. The residual white solid, the diacetate ester of bis-2-β-hydroxyethyl-1-carboranylmethyl) ether, had: mp 116°C; ir (nujol) 2640 (BH), 1760 (C=O), and 1140 cm^{-1} (C-O-C).

I. DIISOBUTYRATE ESTER OF BIS-(2-β-HYDROXYETHYL-1-CARBORANYLMETHYL) ETHER

A solution containing 2.0g (4.8 mmole) of bis-(2-β-hydroxyethyl-1-carboranylmethyl) ether, 4.0 ml of isobutyric acid and 0.6 ml of sulfuric acid in 10 ml of toluene was boiled at reflux in a Dean Stark condenser for 24 hours. At this time the solution was cooled, washed with

V.I (cont.)

sodium bicarbonate solution (2 x 15 ml) and dried (K_2CO_3). The solvent was then removed by rotary evaporation affording white crystalline diisobutyrate ester of bis-(2-β-hydroxyethyl-1-carboranylmethyl) ether: mp 104-108°C; ir 2620 (BH), 1740 (C=O) and 1140 cm^{-1} (C-O-C).

J. MIXED ESTER OF BIS-(2-β-HYDROXYETHYL-1-CARBORANYLMETHYL) ETHER

Methyl succinic anhydride, 0.114g (1.0 mmole) and bis-(2-β-hydroxyethyl-1-carboranylmethyl) ether, 0.836g (2.0 mmole) were thoroughly blended then heated at 100°C for 16 hours. Toluene, 5 ml, containing 0.3 ml of sulfuric acid was then added and the solution refluxed for 4 hours. To the hot reaction mixture was added 5 ml of acetic anhydride. The resulting solution was further heated for 16 hours. Following this heating period, the reaction mixture was cooled, washed with sodium bicarbonate (2 x 20 ml), dried (K_2CO_3) and concentrated by distillation at reduced pressure to the white crystalline mixed ester: mp ∿60°C; the ir spectrum was consistent with the assigned structure.

K. METHYL-BIS-(1-CARBORANYLMETHYL) ETHER

To 16g (0.045 mole) of bis-(1-carboranylmethyl) ether in 150 ml of anhydrous ether, held at 0°C under a nitrogen atmosphere, was added a solution of butyl lithium (0.050 mole) in hexane. This addition was carried out at a rate necessary to maintain a temperature between 10 and 20°C. The reaction mixture was allowed to warm to ambient temperature and 15g (0.11 mole) of methyl iodide was added dropwise. On completion of this addition, the reaction mixture was stirred for one hour and then 100 ml of 10% hydrochloric acid was added. The organic phase, from the resulting two phase mixture, was separated, washed with saturated sodium chloride (3 x 100 ml), dried ($MgSO_4$) and concentrated by rotary evaporation. The resulting white powder was found to be composed of starting material, mono-methylcarborane and di-methylcarborane in a ratio of approximately 1:2:1 (as

V.K (cont.)

determined by nmr analysis). As purification of the desired product proved to present a certain amount of difficulty, it was decided that the reaction mixture obtained would be used for future reaction steps. The physical characteristics obtained on methyl-bis-(1-carboranylmethyl) ether are: mp ∿ 280°C; nmr δ 1.95 (s, 3, $C\text{-}C\underline{H}_3$), 4.05 (s, 2, $C\underline{H}_2\text{-}O$), 4.10 (s, 2, $C\underline{H}_2\text{-}O$) and 4.45 ppm (s(broad), 1, $C\text{-}\underline{H}$).

L. 2-METHYL-2'-HYDROXYETHYL-BIS(1-CARBORANYLMETHYL) ETHER VIII

To 70g (∿ 0.20 mole) of methyl-bis-(carboranylmethyl) ether (as the mixture obtained from the previous reaction) in 1-l of anhydrous diethyl ether was added butyl lithium (0.25 mole as a 15% solution in hexane) while maintaining a temperature between 10 and 20°C. The reaction solution was then stirred for 30 minutes and 8.8g (0.20 mole) of ethylene oxide, as a solution in 100 ml of anhydrous diethyl ether, was added dropwise. After a further 30 min. stirring, the reaction mixture was quenched with 200 ml of water. The resulting two phase mixture was separated and the organic phase washed with saturated sodium chloride solution (3 x 200 ml) and dried ($MgSO_4$). The ethereal solution was then concentrated to a yellowish powder via rotary evaporation. On recrystallization twice from benzene, this powder afforded 32g of white crystalline 2-methyl-2'-hydroxyethyl-bis-(1-carboranylmethyl) ether: mp 188-190°C; ir (KBr) 3350 (O-H), 2870 and 2940 (C-H) and 1130 cm^{-1} (C-O); nmr δ 1.90 (s, 1, $O\text{-}\underline{H}$). 2.28 (s, 3, $C\underline{H}_3$), 2.80 (t, J=8hz, 2, $C\underline{H}_2\text{-}C$), 4.25 (9(overlaping), 2, $\text{-}C\underline{H}_2OH$), 4.50 (s, 2, $C\underline{H}_2O$) and 4.55 ppm (s, 2, $C\underline{H}_2O$).

M. 2-METHYL-2'-CARBOXYMETHYL-BIS-(1-CARBORANYLMETHYL) ETHER IX

In a typical preparation, 3.88g (0.01 mole) of 2-methyl-2'-hydroxyethyl-bis-(1-carboranylmethyl) ether was dissolved in 120 ml of aqueous (15%) acetone (85%) solution and cooled in an ice-water bath. While stirring, 50 ml

V.M (cont.)

of 0.40 N chromic anhydride in 98% sulfuric acid was added slowly, while maintaining a temperature below 15°C. Stirring was continued for an additional hour; then 700 ml of water was added and the solution stirred overnight. The reaction mixture was then further diluted with water (200 ml) and extracted with diethyl ether (3 x 100 ml). The product acid was converted to its sodium salt via washing this ethereal solution with 5% sodium bicarbonate solution (3 x 100 ml). Strangely, the sodium salt of the product acid was insoluble in water and remained in the ether phase. The product was then acidified through washing the ether phase with 20% hydrochloric acid solution. On stripping the ether, a white powder was obtained which upon recrystallization from chloroform gave 3.0g (75%) 2-methyl-2'-carboxymethyl-bis-(1-carboranylmethyl) ether: mp 196.5-197.5°C; neut equiv calc. 402, found 412; ir (nujol), 2620 (B-H), 1760 (C=O), and 1130 cm^{-1} (C-O).

N. 2-METHYL-2'-ACETYLCHLORO-BIS-(1-CARBORANYLMETHYL) ETHER X

To a solution of phosphorus pentachloride 2.1g (0.01 mole) in 8.5 ml of phosphorus oxychloride was added 2.0g (0.0050 mole) of 2-methyl-2'-carboxymethyl-bis-(1-carboranylmethyl) ether. After boiling the reaction mixture at gentle reflux for one hour, the excess phosphorus oxychloride was removed by distillation at reduced pressure. The residue was dissolved in 200 ml of hexane, filtered, and allowed to crystallize by standing overnight at -10°C. Product obtained from this solution was recrystallized from hexane to give 2.0g (90%) of 2-methyl-2'-acetylchloro-bis-(1-carboranylmethyl) ether: mp 129-129.5°C; ir (nujol), 2600 (BH), 1800 (C=O), and 1130 cm^{-1} (C-O).

O. 2-METHYL-2'-ISOCYANOMETHYL-BIS-(1-CARBORANYLMETHYL) ETHER XI

To 50 ml of dry benzene was added 2.0g (0.0048 mole) of 2-methyl-2'-acetylchloro-bis-(1-carboranylmethyl) ether and 4.0g (excess) of sodium azide. The reaction mixture was boiled under reflux for 1 hour during which time gas evolution was noted. On cooling to room temperature, the solution

V.0 (cont.)

was filtered through filter aid and concentrated by rotary evaporation to give the white solid product: mp 135.5-137.5°C; ir (nujol), 2600 (B-H), 2290 (NCO), and 1130 cm^{-1} (C-O); nmr δ 1.98 ($C-C\underline{H}_3$), and 4.44 to 4.48 ppm (s overlapping, 6, $C\underline{H}_2-O-C\underline{H}_2$ and $C\underline{H}_2-NCO$); neut equiv calc 399, found 408.

P. ATTEMPTED THERMAL ISOMERIZATION OF BIS-(1-CARBORANYLMETHYL) ETHER

A glass tube (2.5 x 20 cm), containing 5g of bis-(1-carboranylmethyl) ether, was purged with nitrogen (3 cycle evacuation-nitrogen bleed), evacuated and sealed. The sample was then heated at 400°C for 18 hours. On cooling, the tube was broken and the product removed. This material was dissolved in benzene and eluted through an alumina column (2.5 x 50 cm) with hexane. On concentration of the combined eluents, a white powder was obtained which completely melted at less than 200°C. Sublimation of this material yielded large white crystals which were tentatively identified as methyl-meta-carborane: a sharp melting point was not obtained; nmr δ 2.13 (s, $C\underline{H}_3$) and, 4.60 ppm (s broad, $C-\underline{H}$); ir 3030 (C-H carborane), 2595 (BH). It should be noted that no ether absorption was observed for this material, and that the identical product was obtained when the reaction was carried out at 370°C.

Q. COMPATIBILITY STUDIES

The following is a representative procedure used for the evaluation of compatibilities of alkyl substituted-bis-(1-carboranylmethyl) ethers with HTPB binder systems. A summary of these evaluations is included in the following table.

A sample of R-45M (equiv wt 1338) was mixed with a stoichiometric amount of isophoronediisocyanate (IPDI equiv wt 112). Equal portions of the

V.Q (cont.)

prepolymer and carborane plasticizer were then thoroughly blended and degassed at ambient temperature. When necessary, samples were further blended at 150°F in order to obtain homogeneity and cured for 72 hours at 140°F. The compatibility data are summarized in Figure 7.

VI. CONCLUSIONS AND RECOMMENDATIONS

A. CONCLUSIONS

1. Bis-(1-carboranylmethyl) ether was found to be a valuable nucleus from which useful burning rate catalysts may be derived.

2. Non functional derivatives of the bis-carborane were most useful as burning rate catalysts because high concentrations of these plasticizers can be used in solid propellants.

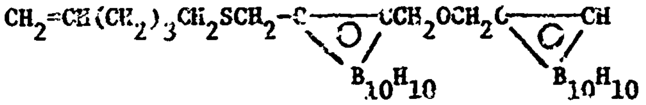
3. Unsaturated and branched-unsaturated substituents were effective at increasing the liquid range of the bis-carborane as well as providing derivatives with improved compatibility in HTPB binders.

4. Functional derivatives of bis-(1-carboranylmethyl) ether, i.e., a diol and a monoisocyanate, were prepared but are marginally useful as burning rate catalysts because of the limited amount of material which can be incorporated into the polymer chain.

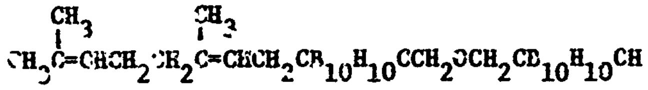
B. RECOMMENDATIONS

1. The undecylenyl-bis-(1-carboranylmethyl) ether, V, and 3,7-dimethyl-2,6-octadienyl-bis-(1-carboranylmethyl) ether, VI, should be fully evaluated in R-45M propellants at several mix and cure temperatures in order to determine the conditions for maximum plasticizer retention.

2. Work should continue on the preparation of new carborane plasticizers such as the cyclopentadienyl-bis-carborane, VII, which likely will have optimum compatibility with HTPB systems. The sulfur derivative, hexenylthiomethylene-bis-(1-carboranylmethyl) ether should also be prepared. This material would be analogous to CMES with a bis-carborane structure.



3. Plasticizers based on meta-bis-(1-carboranylmethyl) ether, such as the dimethyloctadienyl derivative should be prepared and evaluated. The meta-carborane will likely exhibit a wider liquid range than its ortho isomer.



$$CH_3\overset{\overset{CH_3}{|}}{C}=CHCH_2CH_2\overset{\overset{CH_3}{|}}{C}=CHCH_2CB_{10}H_{10}CCH_2OCH_2CB_{10}H_{10}CH$$

4. Carboranes based on pentaborane should be prepared and evaluated, as pentaborane is more economical than decaborane. Suggested compounds are the bis-pentacarboranyl ether and its dimethyl derivative.

$H(C_2B_5H_5)CH_2OCH_2(C_2B_5H_5)H$ $CH_3(C_3B_5H_5)CH_2CCH_2(C_2B_5H_5)CH_3$

REFERENCES

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2. D. Grafstein, et al, Inorg. Chem. 2, 1125 (1963)

3. T. Onak, Advan. Organomet. Chem., 3, 263 (1965)

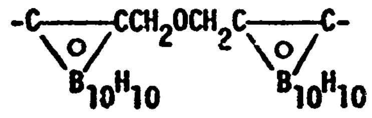
4. G. Stork, P. A. Grieco and M. Gregson, Tetrahedron Letters 18, 1393 (1969).

Enclosure (1)

CARBORANE BURNING RATE CATALYSTS
SUMMARY

INDEX

Z =



1. $H\text{-}Z\text{-}H$

2. $CH_3\text{-}Z\text{-}H$

3. $n\text{-}C_6H_{13}\text{-}Z\text{-}H$

4. $n\text{-}C_9H_{19}\text{-}Z\text{-}H$

5. $n\text{-}C_{10}H_{21}\text{-}Z\text{-}H$

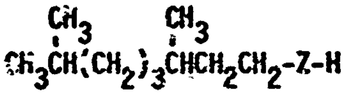
6. $n\text{-}C_{11}H_{23}\text{-}Z\text{-}H$

7. $n\text{-}C_{12}H_{25}\text{-}Z\text{-}H$

8. $n\text{-}C_{13}H_{27}\text{-}Z\text{-}H$

9. $n\text{-}C_{14}H_{29}\text{-}Z\text{-}H$

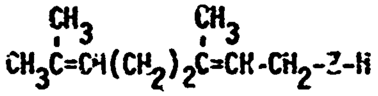
10.



$CH_3\overset{CH_3}{C}H(CH_2)_3\overset{CH_3}{C}HCH_2CH_2\text{-}Z\text{-}H$

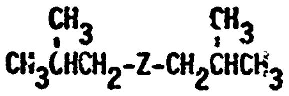
11. $CH_2=CH(CH_2)_8CH_2\text{-}Z\text{-}H$

12.



$CH_3\overset{CH_3}{C}=CH(CH_2)_2\overset{CH_3}{C}=CH\text{-}CH_2\text{-}Z\text{-}H$

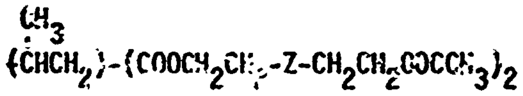
13.



$CH_3\overset{CH_3}{C}HCH_2\text{-}Z\text{-}CH_2\overset{CH_3}{C}HCH_3$

14. $HOCH_2CH_2Z\text{-}CH_2CH_2OH$

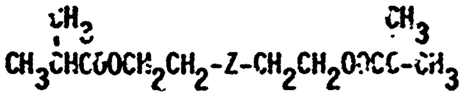
15.



$(\overset{CH_3}{C}HCH_2)\text{-}(COOCH_2CH_2\text{-}Z\text{-}CH_2CH_2OOCCH_3)_2$

16. $CH_3COOCH_2CH_2\text{-}Z\text{-}CH_2CH_2OOCCH_3$

17.



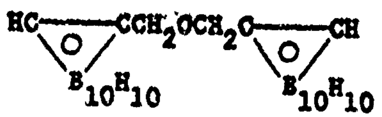
$CH_3\overset{CH_3}{C}HCOOCH_2CH_2\text{-}Z\text{-}CH_2CH_2OOC\overset{CH_3}{C}\text{-}CH_3$

18. $CH_3\text{-}Z\text{-}CH_2CH_2OH$

19. $CH_3\text{-}Z\text{-}CH_2CO_2H$

20. $CH_3\text{-}Z\text{-}CH_2COCl$

21. $CH_3\text{-}Z\text{-}CH_2NCO$



bis-(1-Carboranylmethyl) ether

<u>Physical Properties</u>

(1) Crystalline solid, mp 343-345°C

(2) Boron content, 66%

<u>Characterization</u>

(1) IR and NMR spectra are consistent with the assigned structure.

(2) The melting point is in agreement with the reported value.*

<u>Comments</u> - This is a readily available carborane used as an intermediate in the syntheses of burning rate catalysts. The compatibility of this material with HTPB has not been determined.

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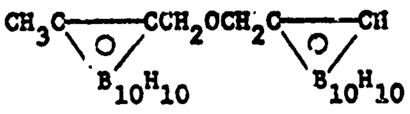
* D. Grafstein, <u>et. al</u>., <u>Inorg</u>. <u>Chem</u>., <u>2</u>, 1125 (1963).



CH_3C—CCH_2OCH_2C—CH ($B_{10}H_{10}$, $B_{10}H_{10}$)

Methyl-bis-(1-carboranylmethyl) ether

Physical Properties

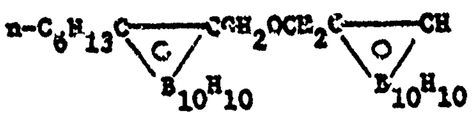
(1) Crystalline solid, mp ~280°

(2) Boron content, 63%

Characterization

(1) The NMR spectrum is consistent with the assigned structure.

Comments - The monomethyl derivative of bis-(1-carboranylmethyl) ether can be used as an intermediate for those syntheses of carborane burning rate catalysts in which only one acidic hydrogen is desirable. The compatibility of this carborane with HTPB has not been evaluated.



n-Hexyl-bis-(1-carboranylmethyl) ether

Physical Properties

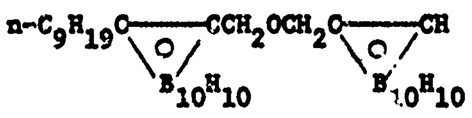
(1) Crystalline solid, mp >50°C

(2) Boron content, 52%

Characterization

(1) The IR spectrum is consistent with the assigned structure

Comments - Compatibility evaluations with HTPB have not been carried out on this compound.



n-Nonyl-bis-(1-carboranylmethyl) ether

<u>Physical Properties</u>

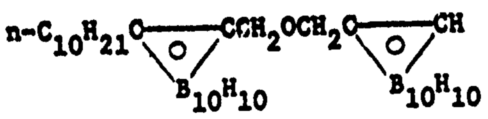
(1) Crystalline solid, mp 45-50°C

(2) Boron content, 48%

<u>Characterization</u>

(1) IR and NMR spectra are consistent with the assigned structure

<u>Comments</u> - The evaluation of this carborane in propellants was carried out at NWC. It was found to be soluble in HTPB but tends to exude from the cured propellant.



n-Decyl-bis-(1-carboranylmethyl) ether

Physical Properties

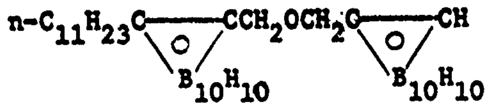
(1) Crystalline solid, mp 23-30°C

(2) Boron content, 45.9%

Characterization

(1) IR and NMR spectra are consistent with the assigned structure.

Comments - The compatibility of this plasticizer was evaluated with R-45M/Isophorone-diisocyanate (R-45M/IPDI). The carborane was found to be between 30 and 40% compatible with the cured binder.



n-Undecyl-bis-(1-carboranylmethyl) ether

Physical Properties

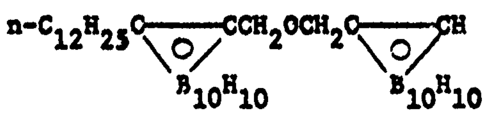
(1) Clear liquid, mp ∿-10°C

(2) Boron content, 44.6%

Characterization

(1) IR and NMR spectra are consistent with the assigned structure.

Comments - This plasticizer was evaluated at the 50% level with R-45M/IPDI. The cured system, although clear and apparently homogeneous, mildly exuded plasticizer. It is felt the compatibility at this level is marginal.



n-Dodecyl-bis-(1-carboranylmethyl) ether

Physical Properties

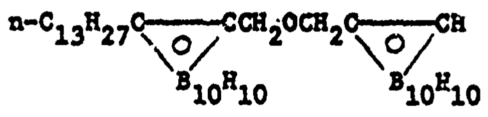
(1) Crystalline solid, mp 25-30°C

(2) Boron content, 43.3%

Characterization

(1) IR and NMR spectra are consistent with the assigned structure.

Comments - This plasticizer was compatible at the 50% level in cured R-45M/IPDI.



n-Tridecyl-bis-(1-carboranylmethyl) ether

Physical Properties

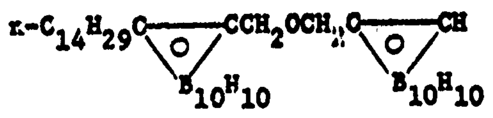
(1) Crystalline solid, mp 30-38°C

(2) Boron content, 42.2%

Characterization

(1) IR and NMR spectra are consistent with the assigned structure.

Comments - On curing at the 50% level with R-45M/IPDI, a clear film was obtained. There was no evidence of incompatibility or plasticizer bleeding at this concentration.



n-Tetradecyl-bis-(1-carboranylmethyl) ether

Physical Properties

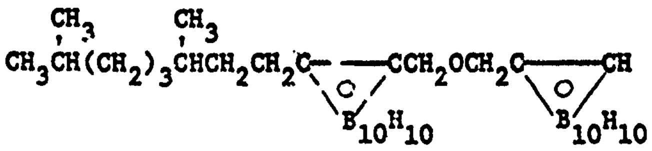
(1) Crystalline solid, mp 35-45°

(2) Boron content, 41.0%

Characterization

(1) The IR spectrum is consistent with the assigned structure.

Comments - The compatibility of this plasticizer with R-45M/IPDI was evaluated at the 50% level. The plasticized polymer was very cloudy and somewhat brittle. This plasticizer is not compatible with HTPB at this level.



3,7-Dimethyloctyl-bis-(1-carboranylmethyl) ether

Physical Properties

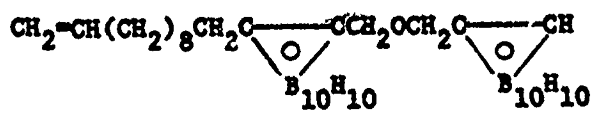
(1) Crystalline solid, mp 66-70°C

(2) Boron content, 45.9%

Characterization

(1) IR and NMR spectra are consistent with the assigned structure.

Comments - On curing at the 50% level with R-45M/IPDI, a cloudy film was obtained. This binder plasticizer mixture does not appear to be compatible at a 50/50 level.



$CH_2{=}CH(CH_2)_8CH_2C{-}CCH_2OCH_2C{-}CH$ (each $C{-}C$ bridged by $B_{10}H_{10}$)

Undecylenyl-bis-(1-carboranylmethyl) ether

Physical Properties

(1) Liquid, mp <-10°

(2) Bp >250°C/1mm

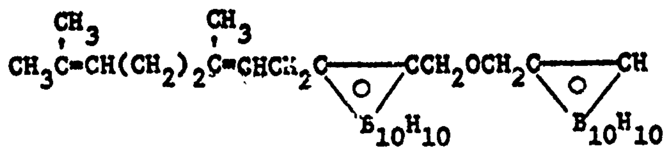
(3) Boron content, 44.8 (calc)

Characterization

(1) IR and NMR spectra are consistent with the assigned structure.

(2) Boron analysis, found 44.7%

Comments - This carborane was evaluated at a 50% level with the R-45M/IPDI binder system. The sample cured to a clear homogeneous film showing no evidence of incompatibility or plasticizer bleeding. A 50g sample of this plasticizer has been delivered to NWC for evaluation in propellants.



3,7-Dimethyl-2,6-octadienyl-bis-(1-carboranylmethyl) ether

Physical Properties

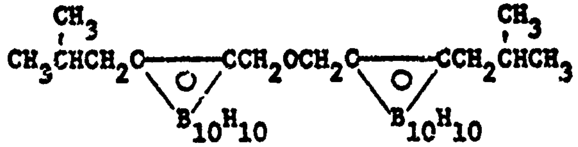
(1) Liquid, mp <-10°

(2) Boron content, 46.3

Characterization

(1) IR and NMR spectra are consistent with the assigned structure

Comments - This plasticizer was found to be compatible with cured and uncured R-45M/IPDI system at equal to or greater than the 57% level. A 50g sample of this carborane is being prepared for delivery to NWC for evaluations in propellants.



bis-(Isobutylcarboranylmethyl) ether

Physical Properties

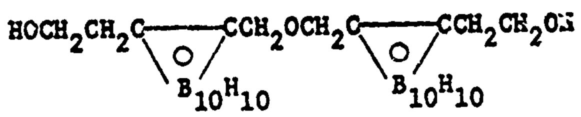
(1) Crystalline solid, mp. >100°C

(2) Boron content, 48.8%

Characterization

(1) The IR spectrum is consistent with the assigned structure.

Comments - Compatibility evaluations with R-45M binder have not been carried out on this compound.



bis-(2-β-Hydroxyethyl-1-carboranylmethyl) ether

Physical Properties

(1) Crystalline solid, mp 125-127°C

(2) Boron content, 55.9%

Characterization

(1) IR and NMR spectra are consistent with the assigned structure.

(2) The melting point is in agreement with the reported value.*

59

Comments - This carborane diol was found to have low solubility in HTPB and therefore considered to be of limited value.

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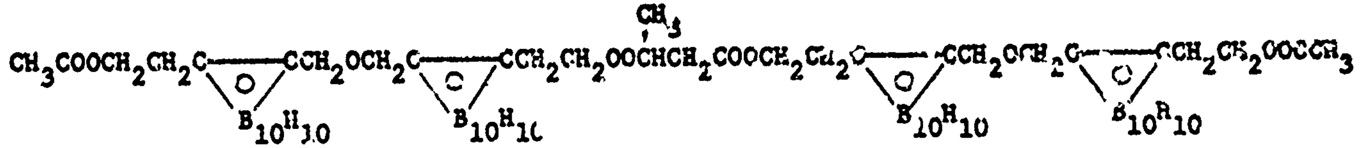
* D. Grafstein, et. al., Inorg. Chem., 2, 1125 (1963).



Carborane Ester Plasticizer

Physical Properties

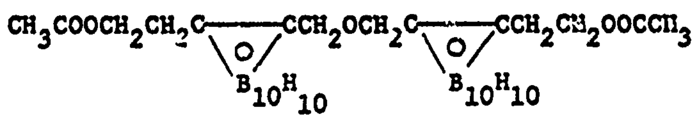
(1) Crystalline solid, mp ~60°

(2) Boron content, 43.0%

Characterization

(1) The IR spectrum is consistent with the assigned structure.

Comments - The compatibility of this material with R-45M has not been determined.



Diacetate ester of bis-(2-β-hydroxyethyl-1-carboranylmethyl) ether

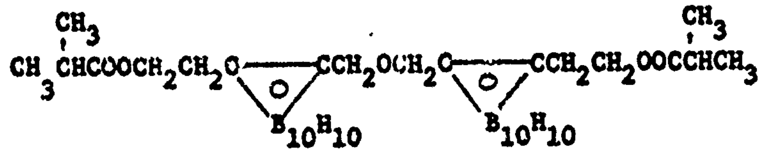
Physical Properties

(1) Crystalline solid, mp 116°C

Characterization

(1) The IR spectrum is consistent with the assigned structure.

Comments - The compatibility of this material with R-45M has not been determined.



Diisobutyrate ester of bis-(2-β-hydroxyethyl-1-carboranylmethyl) ether

Physical Properties

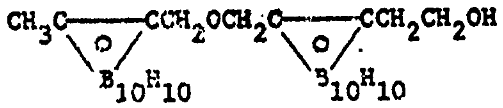
(1) Crystalline solid, mp 104-108°C

(2) Boron content, 38.7%

Characterization

(1) The IR spectrum is consistent with the assigned structure.

Comments - The compatibility of this plasticizer with R-45M has not been determined.



$CH_3C(B_{10}H_{10})CCH_2OCH_2C(B_{10}H_{10})CCH_2CH_2OH$

2-Methyl-2'-hydroxyethyl-bis(1-carboranylmethyl) ether

Physical Properties

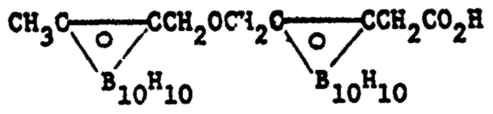
(1) Crystalline solid, mp 188-190°C

(2) Boron content, 55.6%

Characterization

(1) IR and NMR spectra are consistent with the assigned structure

Comments - The compatibility of this monofunctional carborane with R-45M has not been determined.



2-Methyl-2'-carboxymethyl-bis(1-carboranylmethyl) ether

Physical Properties

(1) Crystalline solid, mp 196.5-197.5

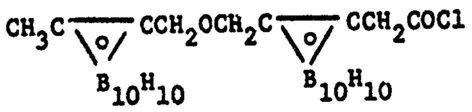
(2) Boron content, 53.7%

Characterization

(1) IR and NMR spectra are consistent with the assigned structure.

(2) Neutralization equivalent calculated 402; found 412

Comments - The compatibility of this material with R-45M binder has not been evaluated.



$$CH_3C\overset{\backslash o /}{—}CCH_2OCH_2C\overset{\backslash o /}{—}CCH_2COCl \quad (B_{10}H_{10},\ B_{10}H_{10})$$

2-Methyl-2'-Acetylchloro-bis(1-carboranylmethyl) ether

Physical Properties

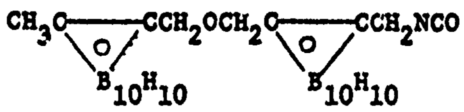
(1) Crystalline solid, mp 129-129.5

(2) Boron content, 51.4%

Characterization

(1) The IR spectrum is consistent with the assigned structure

Comments The compatibility of this material with R-45M binder has not been evaluated.



2-Methyl-2'-isocyanomethyl-bis(1-carboranylmethyl) ether

Physical Properties

(1) Crystalline solid, mp 135.5-137.5°C

(2) Boron content, 54.1%

Characterization

(1) IR and NMR spectra are consistent with the assigned structure.

(2) Equivalent weight calculated 399; found 408.

Comments - A 30g sample of this material has been delivered to NWC for evaluation in propellants.