OLIGOMERISATION OF m-CARBORANE

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Oligomerisation Of *meta*-Carborane

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ABSTRACT

The investigation undertaken in the present dissertation involves the development of a carbon-carbon coupling technique capable of directly interlinking carborane molecules, systematic nomenclature dicarba-closo-dodecaborane (12), as a preparatory stage for future polymeric synthesis of chain structures exclusively composed of carborane units. meta-Carborane finds exclusive use in this study as it presents a more favourable coupling geometry, required in the anticipated future polymerisation investigations, over the ortho-counterpart and is more readily available than the para-isomer. Access to the carbon atoms is essentially restricted to stepwise metallation with either Grignard or lithium reagents, the latter being employed in the present efforts in terms of both a monomeric starting material *per se* and a precursor.

Approaches to the dimeric-m-carborane species, involving standard organic coupling techniques, are profiled in terms of the Ullmann reaction of the diiodinated species of m-carborane with activated copper, direct and catalytically (palladium (II) and copper (II)) promoted ionic coupling of the dilithiated and diiodinated derivatives and metal-assisted reductive coupling of the dilithiated-m-carborane. In summary of these efforts we found the diiodocarborane to be unsuitable for coupling, either alone in the Ullmann sequence, where little or no reaction occurred, or in combination with the lithiated derivative, where the major reaction products appeared to be the result of iodine interference or of oligomer

formation involving the dilithio-carborane alone. The yields and nature of the reaction products led to abandonment of these methods in favour of the more successful metal-assisted coupling of the lithiated species. Employed in these instances were two assist vehicles, the first comprised of a copper (I)/copper(II) system, the second of copper(II). The former system, employing cuprous iodide and cupric chloride, succeeded only in part in affecting dimerisation. The use of cupric chloride alone, however, in the coupling attempts with dilithiated-m-carborane, resulted in sizeable yields of that compound's dimer, i.e. 1,1'-bi-1,7-m-carborane The product, a white crystaline material of mp 271° - 272.2°C was obtained in optimum yields (30% based on isolated and pure product converted from m-carborane) from a system involving the treatment of the solution of lithiated m-carborane with cupric chloride in a tetrahydrofuran medium at low temperatures, (-70°C) and heating to 60°C for approximately 4 hours. Separation and purification were affected by crystallisation from either n-hexane or benzene. Infra-red spectra, although somewhat similar to that for m-carborane, displayed a reduced C-H stretching mode, slight spectral shifts in the fingerprint region and a split breathing mode at 720 cm^{-1}. m/e *circa* 285.

To Carol, Sarah and Jack

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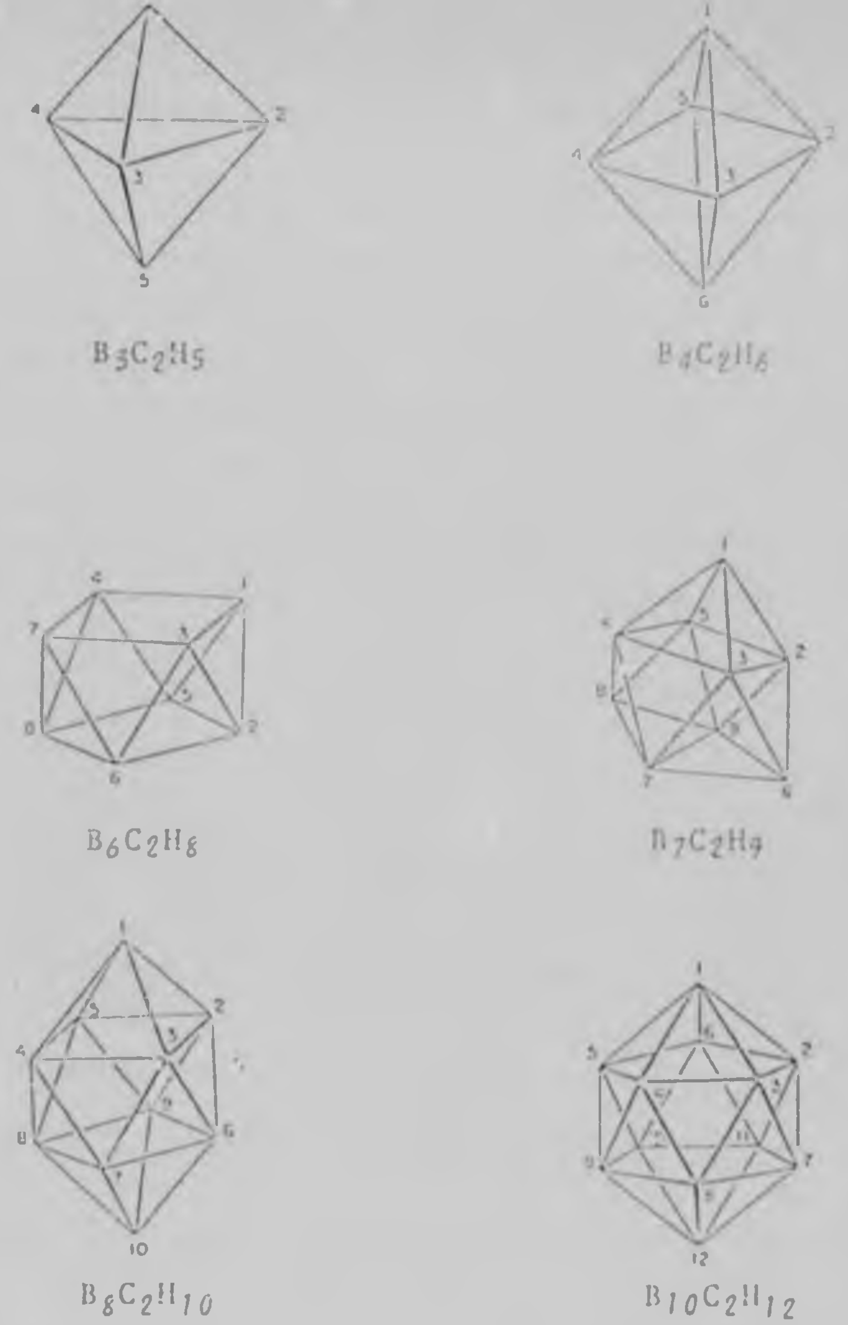
1. INTRODUCTION

The chemistry of the higher boranes and carboranes, a class of highly electron deficient organoboron 'cage' compounds, has over the past 15 years or so developed into a fascinating discipline of inorganic and organometallic chemistry providing challenges to both the theoretical and the experimental researcher. The significance of research into boron cage structures has indeed been recognised recently with the award of the Nobel Prize to William N. Lipscomb, one of the leading pioneers in the field.

Structures of the higher boranes represent open or closed basket-like clusters largely or entirely composed of BH units, which are interconnected by multicenter bonds so as to accommodate the insufficient number of bonding electrons available. Replacement of some (most typically two) of the BH units by CH groups leads to heteroboranes, commonly called carboranes, with little change in structural geometry, but significant alterations of the chemical behaviour. The latter feature renders these carbon-containing species particularly suitable for studies of chemical reactivity. Representative dicarbaborane structures are depicted in Figure 1 As the generic name implies, any two apices in each framework drawing represent CH groups, with the remainder of apex portions occupied by BH units. The molecular formulae thus resulting are given for each drawing.



$B_3C_2H_5$ $B_4C_2H_6$

$B_6C_2H_8$ $B_7C_2H_9$

$B_8C_2H_{10}$ $B_{10}C_2H_{12}$

Figure 1: Some polyhedral cage structures of dicarbaboranes of composition $B_{n-2}C_2H_n$. Two apex positions in each structure are occupied by CH groups, the remainder being of the BH type.

Of outstanding interest among the multitude of known boron cage compounds are the icosahedral dodecaheteroboranes comprising two carbons in place of boron atoms, commonly called dicarba-closo-dodecaboranes. Positional isomerism affecting the two CH members suggests the possibility of existence of three different structures in which the relative sites of CH occupancy are of the 1,2-, 1,7- and 1,12- types. This is illustrated by the structural representations of Figure 2, in which only the carbon and boron atoms are shown for reasons of clarity. In fact, all three isomers are known; contracting the names and using

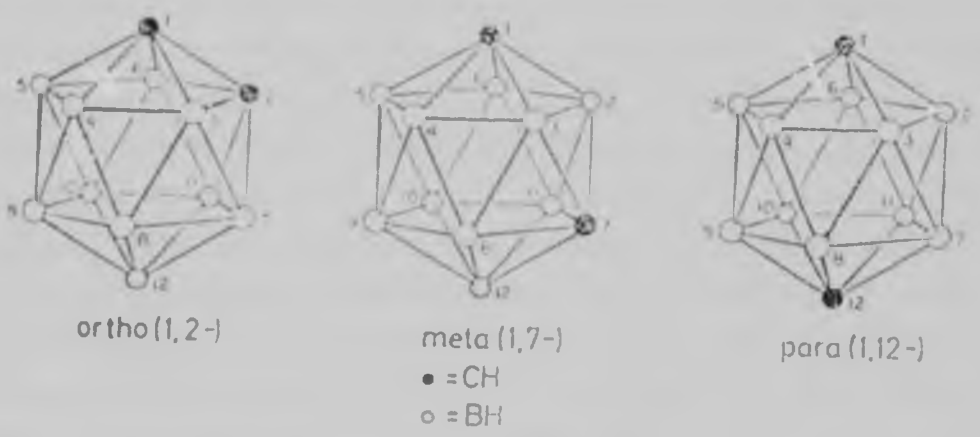


Figure 2: Three isomeric dicarba-closo-dodecaboranes

benzenoid notation of positional assignment, one commonly designates these as ortho-, meta- and para-carboranes.

In view of certain properties of highest technological interest, notably in the fields of high-efficiency rocket fuels, thermal-neutron shielding and heat resistant elastomeric materials, a prime concern of carborane research has been the development of polymeric compounds in which the carborane cluster constitutes a backbone component in the recurring unit. Whilst numerous polymers containing other bridging groups in addition to the carborane cluster have recently been synthesised, no polycarboranes, i.e., polymers exclusively composed of carborane units, are known to this date.

In our attempt to pave the way for the polymerisation of suitable carborane monomers, affording such polymers with directly interlinked carborane groups, the present dissertation effort is aimed at the development of carborane-carborane coupling techniques formally analogous to aryl-aryl coupling procedures familiar to the organic chemist. The substrate isomer chosen for this work is 1,7- dicarba-closo-dodecaborane (meta-carborane), this choice being based on both availability and a suitable polymerisation geometry, i.e., location of the carbon atoms to be involved in the coupling.

The dissertation comprises the following major sections:

- An overview, based on a literature search of the known substitution, interconversion and degradation chemistry of the carboranes, with special emphasis on the *meta*-isomer chosen as the 'work horse' type (section 2);

- A presentation and discussion of the results of the present investigation (section 3);

- A description of the experimental effort of the present investigation (section 4); and

- A summary of the work done as well as conclusions and recommendations (section 5).

2. THE CHEMISTRY OF META-CARBORANE - A LITERATURE SEARCH

2.1 Structure and Bonding. Nomenclature

The history of carborane chemistry can, in essence, be traced to the nido- and arachno-boron hydride structures. As their names imply these open-faced structures assume nest- and web-like skeletal boron arrangements, respectively. Their lattices typically comprise three - centred boron bonds of protonated double bond nature. These compounds generally tend to exhibit a great degree of stability in terms of thermal, oxidative and hydrolytic aspects.[1,3,4,11,12,40] Of special note in this group of compounds is the precursor to the carborane series, decaborane $B_{10}H_{14}$, which is discussed further in § 2.2 in terms of forming the closed cage-like molecular structure by the inclusion of carbon atoms.

Proceeding from the open-faced boron hydrides to the next group of compounds in the discussed hierarchy, one finds the closo-boron hydrides, structurally closed polyhedra described as cage or basket systems.[2,40,11,12,13] The process of cage formation, or conversely, that of cage opening, has been attributed to the addition or removal of electrons to the system, eg., as in redox reactions.[12] Boron-hydride polyhedra assume a variety of structures;

tetrahedron, trigonal bipyramid, octahedron, pentagonal bipyramid, dodecahedron, tricapped trigonal prism, symbicapped square antiprism, hexadecahedron and icosahedron. The latter is of primary importance in this work as the carborane molecules to be discussed, too, conform to this structure.[104]

The boron atoms in these polyhedra have been associated with a large coordination number, up to six, implying an inherent stability in the various structures. Those polyhedron molecules exclusive of boron hydrides exhibit, in addition to the three-centred two-electron bonds of boron, bridged B-H-B hydrogen bonds.[16,104] By molecular orbital theory description, the three-centred two-electron bonds combine three atomic orbitals from three boron nucleii to give three molecular orbitals, of which only one is bonding. These three-centred bonds in boranes imply no real electron deficiency by strict definition as electron deficient molecules, i.e., having more valence orbitals than electrons. A formal charge of -2 is assigned to borohydrides, B_nH_n for n of 5 to 24, even though B_4H_4 is neutral.[14] The boron hydride polyhedra thus exhibit a fairly significant degree of resonance stabilisation. Their electronic natures have been associated with an aromatic type behaviour, reflected in their relative stabilisation over their 'non-aromatic' arachno- and nido-borohydride counterparts.[4,104,40]

The introduction of carbon atoms into borane systems to yield polyhedral carbon-boron structures gives rise to a novel class of organometallic compounds, broadly termed carboranes. The general rule applicable to the carboranes, $C_2B_{n-2}H_n$, is that they conform to an n-vertex polyhedral structure.[12] The name carborane, however, is more often associated specifically with the *ortho*-isomeric form of the $C_2B_{10}H_{12}$ molecule. The systematic nomenclature for this compound is 1,2- dicarba-*closo*-dodecaborane(12), alternatively referred to as barene or, in older works, as dicarba-*clovo*-dodecaborane. The shorthand notation to be employed for this compound will be; *o*-HC-$B_{10}H_{10}$-CH. Similarly, the *meta*-carborane isomer, 1,7- dicarba-*closo*-dodecaborane(12), or neo-barene, will assume the notation *m*-HC$B_{10}H_{10}$CH and the *para*-isomer, 1,12- dicarba-*closo*-dodecaborane (12), will be referred to as *p*-HC$B_{10}H_{10}$CH. The *ortho*-carborane *o*-HC-$B_{10}H_{10}$-CH molecule assumes a distorted icosahedral structure of C_{2v} symmetry, which is isoelectronic and isostructural with the $B_{12}H_{12}^{2-}$ borane molecule, although this borane assumes I_h symmetry.[3,4,5,10,14,102,104]

The carborane crystal is found to have a face-centered cubic cell containing four molecules. The carboranes thus satisfy structural criteria for plasticity.[102]

In terms of electronic behaviour, similarities can be drawn between the carboranes and closed borohydride polyhedral systems. For the closed borohydride polyhedral systems, B_nH_n with $n \geqslant 5$, the $2_n + 2$ rule is adhered to. The rule assumes that $2_n + 2$ valence electrons are required to fill the bonding molecular orbitals of the cage. These systems therefore lack sufficient electrons to describe all nearest neighbour interactions in terms of two-centre two-electron bonds and thus require some degree of delocalisation.[20] All cage molecules adhering to the $2_n + 2$ rule are formally deficient of electrons. Extension of this rule encompasses the case of the carborane molecules, which experience more extensive delocalisation in the additional considerations of the electropositive carbons and the two additional electrons present. The resultant carborane structure is highly resonance-stabilised and thus referred to as assuming "super-aromatic" characteristics.[4,16,19,20,61,104,36] However, unlike $B_{12}H_{12}^{2-}$, carboranes bear no formal charge, but an asymmetry of charge exists because of these electropositive carbons.

2.2 Chemistry of Formation

The fundamental reaction leading to the carboranes involves condensation of decaborane ($B_{10}H_{14}$) and acetylene in the presence of a ligand, like e.g. diethylene sulphide.[10,11,15,16,104] The reaction yields the *ortho*-isomer of carborane, 1,2-dicarba-*closo*-dodecaborane (12) (the 12 indicating the number of hydrogens present in the base molecule), by undergoing rapid isotropic molecular reorientation in the high-temperature phase (determined by ^1H NMR).[102] Purification of the product is accomplished by sublimation and followed by recrystallisation from normal aliphatic solvents.

The *meta*-carborane isomer, m-HC-$B_{10}H_{10}$-CH, is obtained from o-HC-$B_{10}H_{10}$-CH by irreversible thermal rearrangement at 450° - 500°C.[4,10,13,17,18] It has similarly been determined that rearrangement processes for carbon and boron mono - and di - substituted carboranes proceed irreversibly from *ortho*- to *meta*-forms.[113] Isomeric rearrangement has been found also to occur with carboranes dianion species, but in the reverse order to that of the neutral carboranes, i.e., *para* to *meta* to *ortho*. The process is these instances, however, involves a degree of boron bonding, and the mutual repulsion of the negative charges is assumed to be the reaction's driving force.[18] The rearrangement process is thought to occur via a cube octahedron intermediate, a low energy process, with the charged C^+ atoms providing the driving force to the m-$HCB_{10}H_{10}CH$

species.[104] The resultant meta-carborane occurs as a distorted icosahedral molecule and like its ortho-counterpart, assumes C_{2v} symmetry.[5,13] In the latter instance, the C-C single bond delocalises to the two borons adjacent to the carbons. In the former, the B-B single bond, situated between the carbons, delocalises to two fractional centres (i.e., electron deficient borons).

From thermodynamic considerations, it would be expected that the separation of the active carbon sites, by interspacing with borons, in the m-HC-$B_{10}H_{10}$-CH molecule would lead to a more stable isomer over the o-HC-$B_{10}H_{10}$-CH case.[5,6,64,112] Studies by Zakharkin [113] have given rise to the following enthalpies of formation in support of the above:

ΔH (298)(g) for o-HC-$B_{10}H_{10}$-CH = 6.31 kJ/mol.

ΔH (298)(g) for m-HC-$B_{10}H_{10}$-CH =10.12 kJ/mol.

The final carborane isomeric form is p-HC-$B_{10}H_{10}$-CH. The para-molecule is derived from m-HC-$B_{10}H_{10}$-CH by thermal rearrangement at 650° -700°C via a reversible equilibrium process.[115] This isomerisation process has been hypothesised as occurring via a pseudo-rotation of the skeleton with triangular face B_2C rotation. The driving force is provided again by charged C^+ atom repulsion, but to a far lesser degree than in the ortho-to *meta*-case.[104] Additionally, a certain degree of skeletal degradation is likely to occur during the transformation. The resultant *p*-$HC-B_{10}H_{10}-CH$ structure appears as an elongated icosahedron of C_s symmetry, also via a cube octahedron intermediate.[8,10,13,17,18,104] In the latter structure three fractional centres exist, two in the upper pentagon, one in the lower. Three delocalised single bonds, one of B-C and two of B-B type, donate to these sites. The B-C bond connects the apex to the pentagon, the two B-B's connect the two pentagons. The separation of the electropositive carbon sites in this molecule renders it the most stable of the carborane forms, with enthalpies of formation only marginally lower than those for the *m*-$HC-B_{10}H_{10}-CH$ isomer.[19,113]

The active sites of the carborane cage system are the very positive carbon atoms. Their electron donation to the withdrawing boron cluster results in the assignment to the carbons of unusually high coordination numbers of up to six. Both the boron and carbon atoms in the molecule appear effectively sp hybridised.[40,12] The carbon atoms, as would be expected, readily deprotonate, and access to the cage at these sites is generally achieved by stepwise metalation with lithium or Grignard reagents.[6,9,10,14,61] The electron deficient boron skeleton determines the protonic mobility of the C-H group, indicating a reduction in acidity can be expected from the *ortho*- to the *para*-isomers by virtue of the spatial separation of these sites.[105,112] Organic functional groups attached through their carbons to the carborane molecule are furthermore found to be strongly electron withdrawing.[10] However, in comparison to decarborane, the carboranes *in toto* demonstrate a reduced acidity. The increased acidity of the borohydrides is attributed to the presence of the bridged hydrogen content of these molecules.[16]

The varying degrees of acidity amongst the three isomeric forms of carborane provide, with chromatography, a convenient means of separation of the individual forms.[8,12,104] This factor further manifests itself in a drop in melting points of the isomers in accordance with a polarity reduction from ortho through para, as well as a slower metalation rate at the respective carbon sites.[6,7,9,12,19] The dipole moment found for $\underline{o}\text{-HC-B}_{10}\text{H}_{10}\text{-CH}$ is 4.31 D, that for $\underline{m}\text{-HC-B}_{10}\text{H}_{10}\text{-CH}$ is 2.78 D, and $\underline{p}\text{-HC-B}_{10}\text{H}_{10}\text{-CH}$ is naturally unpolarised.

The nature of the carbon atoms in the carborane nucleus renders the molecules impervious to attack by compounds with active hydrogens and, furthermore, renders them incapable of attacking reducible groups such as carbonyl or nitrile.[13,15,34] The nucleus itself is comparatively inert and reactions of the molecule are, for the most part, limited to the functional groups attached to carbon. Thermal stability, resistance to solvolysis, acids, weak bases, air-oxidation and general chemical degradation are demonstrated by the nuclei.[6,29,19]

2.3 Substitution Reactions on Boron

The behaviour of boron in the carborane systems is very similar to that of a carbon in purely organic compounds.[113] Reactions pertaining to the boron atoms include electrophilic and nucleophilic substitution at these sites, photochemical substitution and actual boron abstraction. Electrophilic substitution reactions at boron in general tend to occur at those sites farthest removed from the carbon atom locations, whilst the converse holds true for nucleophilic substitution.[14,19,61,104] In comparison to the polyhedral boranes, however, a greater degree of resistance to, eg., electrophilic attack is noted with those B-H bonds of neutral carboranes even at elevated temperatures.[104] Electrophilic halogenation of the carborane compounds occurs exclusively at the boron sites as opposed to the carbon sites. Not unexpectedly, the rates of halogenation are greatest with the $\underline{o}$-HC-$B_{10}H_{10}$-CH and lowest in the case of $\underline{p}$-HC-$B_{10}H_{10}$-CH. The primary attack site in, eg. $\underline{o}$-HC-$B_{10}H_{10}$-CH, would be in position B-9.[105,107] Reduction of $\underline{o}$-HC-$B_{10}H_{10}$-CH occurs more readily than that of $\underline{m}$-HC-$B_{10}H_{10}$-CH, because of the greater electron affinities of the former over the latter. Similar trends can be noted in the case of m-HC-$B_{10}H_{10}$-CH with respect to $\underline{p}$-HC-$B_{10}H_{10}$-CH, the latter having the weakest electron withdrawing effects of the carborane isomers and, therefore, the greatest resistance to nucleophilic attack.[18,63]

Boron-halogen bonds in halogenated carborane derivatives tend to be extremely stable, but are capable of entering into nucleophilic substitution reactions.[48,59] An example of this reaction type is that of the formation of a cyano-derivative, in position B-9, from the 9-iodo-o-HC-$B_{10}H_{10}$-CH in the presence of CuCN.[110] Sulfhydrylation will also occur in m-HC-$B_{10}H_{10}$-CH the most negative boron atom giving 9-HS-m-HC-$B_{10}H_9$-CH.[10]

The determined electron-attracting effects of the carborane nucleus decrease in the order:

$1>3>4>8>9$ for o-HC-$B_{10}H_{10}$-CH and:

$1>2>4>5>9$ for m-HC-$B_{10}H_{10}$-CH.

Isomerisation of, eg., 3 cyano-o-HC-$B_{10}H_{10}$-CH yields two products of the meta isomer, *viz.* 2 cyano m-HC-$B_{10}H_{10}$-CH and 4-cyano-m-HC-$B_{10}H_{10}$-CH. This holds true for amino-, hydroxy-, carboxy-, fluoro- and diphenylamino- substituents. The chloro-substituent however produces meta-isomeric products in the 5 and 9 positions from the 3 substituted position of the ortho-compound.[110,28]

Other reactions involving the boron sites of the carboranes would include oxidation, which yields B-hydroxy carboranes, with isomer formation directing the hydroxyl groups such that they are farther removed from the carbon locations of the molecule.[110] Photochemical substitution too is limited to the boron atoms within the carborane framework.[14] Fluorination of the ortho-, meta-and para-carboranes yields only $B_{10}F_{10}C_2H_2$ with respect to the three isomeric forms. Hydrolysis of these perhalides has been performed easily unlike in other halo-carboranes.[00] The action of removing one boron atom from the carborane can be accomplished in the presence of a strong base in an alcoholic medium.[19,84] Stability towards strong bases increases from the ortho- to the meta- to the para-isomer.[105]

Boron-substituted metallic derivatives of carboranes can be obtained by, eg., mercuration, using mercury trifluoroacetate in trifluoroacetic acid, a reaction that progresses at room temperature. These B-mercurated carboranes provide a convenient starting compound for the synthesis of group IV to VI element derivatives of carborane. Examples of these would be Sn, As, Sb and S bonded through boron.[106,107] An additional noted reaction is that of thallium transfer to the B-9 position of mercurated carboranes with thallium (III) trifluoroacetate.[108] Transition metal derivatives, eg., Fe and Re, and the ferrocene analogues have been prepared with the metal-boron bonds as opposed to metal-carbon.[93,113] Yet an additional class of metallic derivatives, the metallocarboranes involve metal-boron bonds. These compounds are generated by the aforementioned base degradation of the carborane nucleus and involve insertion of the metal ions into the $B_9C_2H_{11}^{2-}$ vertex followed by hydride ion reduction.[104]

The final type of boron bonding occurs in the instances of the dicarborane compound, a dimer coupled via a boron-boron bond by the action of copper in tetrahydrofuran. The dicarborane found by Stanke et al, 9,9'(10,10')-di-m-HC-$B_{10}H_{10}$-CH had a characteristic melting point of 182° -183°C and was found to be readily soluble in aromatic hydrocarbons.[48] Treatment of dinido-carborane, $C_4B_{18}H_{22}$, with B_2H_6 also yields the dicarborane compound as well as o-HC-$B_{10}H_{10}$-CH.[54]

2.4 Substitution Reactions on Carbon

The principle means of selective access to the carborane nucleii at the reactive carbon sites is *via* stepwise metalation with either lithium or Grignard reagents, as mentioned in Section 2.2. One other method of achieving direct access to these carbon sites exists, but has had limited success in so far as that only the ortho-isomer undergoes reaction. This reaction involves the treatment of o-HC-$B_{10}H_{10}$-CH with organomercury hydroxides. The failure of m- and p-HC-$B_{10}H_{10}$-CH to react has been attributed to the reduced hydrogen acidity of those isomers.[111]

The lithium and Grignard intermediates of carborane are extremely reactive to a host of organic and inorganic reagents. In the case of Grignard reagents however, primary alkylates form only with extreme difficulty.[21,104] The degree of metalation substitution is determined by the equilibria established, shifting to the left as the acidities decrease in the meta and para instances.[21,22]

Halides comprise the simplest and easiest formed carborane derivatives, giving rise to both mono- and di- substituted compounds. The relative reactivities of the halides formed decrease in the order I > Br > Cl.[47] Mono- and di-iodo-carboranes form readily from the mono- or di-lithiated derivatives, respectively, by iodination with either chlorine mono-iodide or solid iodine in a non-polar organic solvent medium.[8,35,19,23,112] The positive nature associated with the iodine gives rise to a C-I bond in carborane which is readily reduced. These derivatives conveniently supply the starting-blocks, in the form of anions, for coupling reactions. (Refer to Section 2.5). Of particular importance is the white, plate-like crystalline m-I-C-$B_{10}H_{10}$-C-I (mp 74°-75°C) employed in this work. Unlike its ortho-counterpart the meta-isomer is restricted by its geometry from forming exopolyhedral rings, thus opening the possibilities of its polymerisation.[22,104] The replacement by hydrogen in the presence of nucleophilic reagents is likely to occur with the iodo-carboranes, whereas the same would not hold true for the substantially more negative chloro-compounds.[7] In addition to alkali, the reduction of iodine to give carborane is effected by alcohols, water, ether, aluminum oxide and lithium.[22,23,24] The synthesis of chlorocarboranes is accomplished in a similar fashion to the abovementioned iodo-compounds, only employing gaseous chlorine in the reaction. The chlorine, as intimated, will increase the acidity of the carboranes as well as the stability of the carboranyl anions.[112] As with the other halo-derivatives the chlorine compounds have the properties of being readily distillable and very soluble in organic solvents. They are, additionally, hygroscopic.[22]

Another class of derivatives found to be particularly useful is that of the carbinols, an example being the m-dihydroxy compound, $m\text{-HO-C-B}_{10}\text{H}_{10}\text{-C-OH}$, which is a white crystaline compound of mp 194° - 196°C.[6] Synthesis can be conducted by a number of methods, the easiest and most common being the treatment of the dilithio-species with oxygen and subsequent hydrolysis.[25] Other methods leading to carbinols entail treating the lithiated derivatives with paraformaldehyde or ethylene oxide.[4,19,29] Secondary and tertiary alcohols are also readily obtainable, eg., by the reaction of esters or aldehydes with the lithiated carborane derivatives.[26,41] Oxidation of the hydroxycarboranes yield ketones or esters.[4,27] The ketones in turn are readily reduced to the alcohol derivatives and readily undergo C-C cleavage in the presence of bases.[7,26,41,50]

The alcohols will revert to unsubstituted carboranes, however, when oxidized with aqueous alkaline potassium permanganate.[5] Ester formation can additionally be achieved by treatment of the lithiated carboranes with, eg., acetyl chloride or *via* the reactions of acetylenic compounds with acetonitrilo-decaboranes.[16,26]

The action of carbon dioxide on the lithiated carborane species readily produces the carboxylic acid derivative. In the instance of *m*-$HO_2C\text{-}C\text{-}B_{10}H_{10}\text{-}C\text{-}CO_2H$, the compound formed is a white crystalline material of mp 202° - 204°C. As with the carboxylic acid derivatives in general, it remains stable unless heated in aqueous solution, whereupon decarboxylation occurs.[4,6,7,19] The action of phosphorous pentachloride upon the carborane carboxylic acid compounds gives rise to the acid-chloride derivatives. The diacid-chloride compound, *m*-$C\ell CO\text{-}C\text{-}B_{10}H_{10}\text{-}C\text{-}COC\ell$, bp 86°/4mm Hg, can be produced either via the above method or alternatively directly from the dilithiated *m*-carborane. The dilithio compound upon treatment with phosgene yields the abovementioned, whereas the same treatment of dilithio-*o*-carborane leads to the diketo-dimer of that compound.[51]

Employing carborane acid chlorides in hydrogenation reactions over a palladium catalyst results in the formation of aldehydes of carborane. Other methods reported for the preparation of these derivatives include ozonization of vinyl carborane, the ethoxy-methylaniline reaction with lithio- or magnesio-carboranes, and, in the case of o-carborane, the mild oxidation of its alcohol with dimethyl sulfoxide.[19,40,41,45] C-formyl-m-carborane, m-$HC-B_{10}H_{10}-C-CHO$, mp. 213°-214°C, and C,C'-diformyl-m-carborane, m-$OHC-C-B_{10}H_{10}-C-CHO$, mp. 164°C, occur as white crystaline solids. These aldehydes undergo cleavage in the presence of bases and only slowly react with 2,4-dinitrophenylhydrazine.[40,42,115]

Additionally, the lithiated carborane compound will undergo substitution reactions to form anilides, cyclic dicarboxylic anhydrides,(ortho), as well as mercuric-, phospha- and sila-derivatives.[4,26,51,57,112,53] Transition metal complexing, especially with copper, nickel and cobalt, employed as Cu^{III}, Cu^{II}, Ni^{III}, Co^{III} and Co^{II}, have also been reported to occur with the carboranes.[52,98,20]

2.5 Coupling Reactions Involving Carboranes

Coupling of carboranes can be simply classified into categories of direct and indirect reactions. Functional-group interspacing of the carboranes, leading to a range of products, from dimeric through oligomeric to polymeric materials, has been investigated fairly extensively. On the other hand direct - type coupling of the carboranes remains largely unexplored. Within this latter category of coupling reactions we confine ourselves to linkage of the carborane molecules to each other *via* the establishment of C-C bonds of the carborane's carbon atoms. The linkage is most commonly established in the reaction involving iodo-carboranes with activated copper, i.e., Ullmann-type synthesis.[48,52,96,97,99] Dimeric products of both the ortho- and meta- isomers have been obtained by this method. As with pure organic compounds, the halide derivative employed is the iodide for reasons of its reactivity, the reaction commencing *via* nucleophilic attack of copper facilitated by the electron withdrawing carborane nucleus. The second stage in the reaction is the nucleophilic attack of copper complex on the second halide compound. The copper catalyst can be prepared and activated by several methods, and it is thought to give rise to an intermediate of oxidation state III.[31,32,33,44,45,47,49,52,96] A less common method of producing the dimer *via* the reaction of diacetylene with the $B_{10}H_{12}(CH_3CN)_2$ has been reported. C-ethinylcarborane is additionally formed during the process, and the reaction is necessarily applicable only for the preparation of the ortho-carborane dimer.[46] As yet unreported is the formation of oligomeric carboranes by the Ullmann reaction or the use of alternative metal catalysts, eg., nickel.[45]

Formation of biscarborane compounds with ketonic or diketonic linkages (reaction of the carboxylic acid chloride with the lithio-derivative), dicarboranyl ether, carboranes linked by organometallics, eg., ferrocene, and by metal atoms, eg., mercury, broach the alternative indirect linkage systems of the carboranes to each other.[12,13,50,92] Extension of coupling reactions beyond the dimer stages to polymeric systems containing various organic and inorganic linkages have been extensively explored. Successful synthesis of poly-carboranyl esters, formals, urethanes, amides, imides, phenylenes, xylenes, arylates, acrylates, ureas, and olefins have been accomplished in the organic sphere and, on the inorganic side, various silicon, germanium, tin, lead, phosphorous and sulphur polymeric linkages have been utilised with carborane compounds.[4,19,55,56,58,59,61,64,68,70,77,83] The polymers so formed generally tend to be soluble in most common organic solvents and, with the exception of some nitrogen-containing linkage systems, exhibit an excellent degree of thermal stability.[62,63,70,78,79,80,104]

The polyamides of carborane are in part susceptible to degradation at elevated temperatures and oxidative cleavage. The amide bond tends to undergo both heterolytic and homolytic decomposition in these instances.[63] Instability has in part been associated with the weak dicarbaundecaborane intermediate formed during aromatic polyamide synthesis.[69] The thermal ageing process of the polyamide(NH) additionally appears to be related to the electronic effects between the carborane cage and the amide N. The unpaired electrons of nitrogen, in a conjugated carborane amide system, are attracted to the electronegative carborane nucleus. This has the effect of destroying the system's equilibrium, leading to degradation. By introducing intermediate groups such as a carbonyl or phenyl between the amide nitrogen and the carborane weakens these electron influences and enhances stability.[73] Within the isomeric forms of carborane itself, the electronic interactions give rise to greatest stability in the para-, and lowest stability in the ortho-case. Thermal-oxidative resistance, softening temperatures, and solubilities all are higher in accordance with this order in individual polyamides.[64,74] A thermally stable class of these compounds has evolved from the selective employment of suitable linkage systems, the establishment of cross-linking sites and, finally, by modifications to hydroxyamide functionalities.[63,68,71,74]

The polyimides of carborane, which are derived from carboranylene diamines, demonstrate a low resistance to heat. The presence of dicarbaundecaborane units in these polymers is thought again to be the cause of the thermal and hydrolytic instabilities as well as the low polymer viscosity.[72] Polyimide formation has thus far been achieved only with the *meta*- and *para*-isomers owing to the steric effects of the carborane substrate and the linkage systems greatly influences the chain flexibility, forming, extremely rigid structures similar to the polyarylates.[67,85] As in the case of the polyarylates of carborane where, at approximately 350° to 400°C, the carborane nucleus itself accelerates the degradation of the polyester and, at approximately 450°C, is transformed into a thermally stable structure, so a parallel behaviour is observed with the other carborane polymers, including those of the stabilised amides within the organic type linkage systems.[19,62,74,75,78]

The most important member of the polymer family of carboranes employing inorganic linkage systems is the class of the siloxanes. Polymers of this class are formed by condensation polymerisation and comprise of linear long chain structures. The best known examples of the carborane polysiloxanes are the Dexsils (Olin), finding applications as high-temperature specialty adhesives. Because of steric effects, the *meta*-isomer of carborane more readily gives rise to these compounds than would the *ortho*-counterpart. Elastomeric properties are obtained from the polymer class when modified with a trifluoropropyl group, for example. These again form linear high molecular mass compounds of similar properties to the above.[19,76,81,82,37,38,100,101,103]

Aside from silicon, the other group I. b elements (Ge,Sn,Pb) have been known to form polymeric structures with carborane.[55,56,59] Phosphorous, phosphorous-nitrogen (P-N-P), silicon - oxygen and sulphur linkages employed with polymeric carboranes form the remaining bulk of the plastics family.[56,61,80] Amongst these products those with *meta*- and *para*-carborane in the backbone are prevalent,because of steric problems of the *ortho*-isomer.[58]

[illegible] Spectroscopic Features

A quantitative guide pertaining to the carborane chemistry dealt with in this work has been obtained from the listed spectroscopic reports. The primary analytical tool employed lies with infra-red spectroscopy,while nuclear magnetic resonance and mass spectroscopy are employed to a far lesser degree. Mass spectroscopic patterns of *closo*-borohydrides and carborane series invariably provide high-intensity parent ion peaks with second and third generation ions of greatly reduced intensities.[6,86,89,90] than would the ortho-counterpart. Elastomeric properties are obtained from the polymer class when modified with a trifluoropropyl group, for example. These again form linear high molecular mass compounds of similar properties to the above.[19,76,81,82,87,88,100,101,103]

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Nuclear magnetic resonance of ^{11}B for the ortho- and meta-isomers gives rise to four doublets, the intensities varying in accordance with the differing boron geometries. With the ten geometrically equivalent borons of the para-isomer, only one ^{11}B NMR peak results.[91] The ^{1}H NMR of carborane gives rise to only two singlets of C-H, and, at very high resolution, four broad peaks of B-H can be observed.[4,19,87,91]

Infra-red data for the carboranes can be summarized by the following scheme. The B-H stretch mode appears at 2600 cm^{-1} (from 2560 cm^{-1} for $B_{10}H_{12}$), and bending occurs at 1000 cm^{-1}.[63,88] For ortho-carborane C-H stretch appears at 3080 cm^{-1}, a H-C-C bond vibration mode gives bands at 1150 and 1200 cm^{-1}, and the cluster breathing mode leads to a band at 750 cm^{-1}.[4,87] Meta-carborane exhibits one deformational single valence C-H vibration at 1160 cm^{-1}. The 1200 cm^{-1} band is absent, and remaining peaks emerge at 1160, 1070, 1020 and 990 cm^{-1}.[6,85,87] The breathing mode, likewise, shifts to 720 cm^{-1}. The para-derivative, too, shows significant differences in the 1300 to 850 cm^{-1} range.[114] In the carborane dimers, a shift of the C-H stretch occurs to 3040 cm^{-1}.[48,52] The effects of halogen substituents on the carboranes is noted in the form of splitting of the B-H vibrations at 2650 and 2590 cm^{-1} For mono-halo-carboranes, the C-H stretch is increased in intensity.[22,48,60] Aldehyde groups are characterised by a 1750 cm^{-1} peak whilst other carbonyls occur at 1720 cm^{-1}.[40,51]

Finally molecules in which the carborane cluster is combined with other moieties, such as the ferrocene complex, give rise to superimposed spectral prints in accordance with their respective structures.[92,94,95]

3. RESULTS AND DISCUSSION

3.1 Objectives and Scope of Dissertation

The principle objective of this work lies in the development of a direct carbon-carbon coupling technique capable of effectively synthesising the dimeric-carborane compound. As the results will have potential bearing upon future synthesis of strictly carborane backbone constituent oligomeric and polymeric materials, the described efforts are restricted to the coupling of the 1,7- isomer, i.e., *m*-$HC-B_{10}H_{10}-CH$, to form bi-1, 7- dicarba-*closo*-dodecaborane(12) (see figure 3). The exclusive use of the *meta*-carborane compound in these works is based upon the fact that it demonstrates a more favourable coupling profile over its *ortho*-counterpart in terms of intramolecular carbon geometry and, additionally, is more readily available than the *para*-isomer.

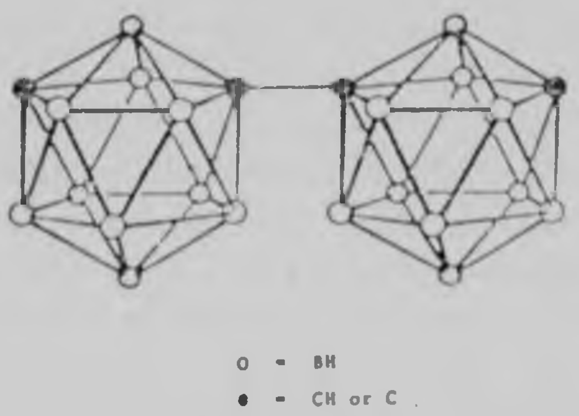


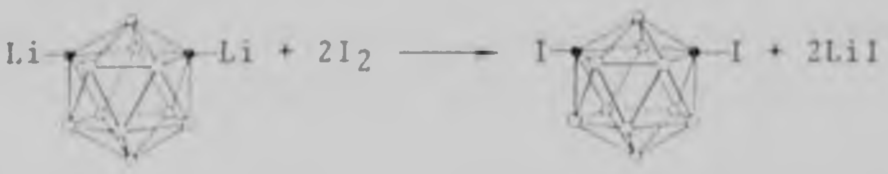
Figure 3: Ball and Stick Representation of bi-1, 7-dicarba-*closo*-dodecaborane(12)

Since no known means of achieving higher oligomeric and polymeric structures of the carboranes *via* direct coupling of their carbon atoms exists to date, it is believed this research will prove valuable in areas related to their manufacture in terms of thermo-nuclear shields, high-performance rocket fuels and specialty adhesives. The benefits of linear-chained polymeric compounds comprising directly interlinked carborane units, over those molecules composed of indirectly linked cluster molecules, will be immediately evident in their neutron capture capabilities as well as the possibilities of exhibiting superior mechanical, thermal and chemical performances.

Dimerization approaches undertaken in this dissertation, employing formal organic coupling processes with m-carborane, include the Ullmann reaction employing diiodo-m-carborane, discussed under section 3.2, the unaided coupling attempts employing dilithiated and diiodinated carboranes, dealt with in section 3.3, the use of a palladium(II) catalytic system with the two aforementioned derivatives, contained in section 3.4, and a repeat of the catalytic approach substituting the palladium by a copper(II) system, discussed in section 3.5. Section 3.6 entails the coupling attempts using dilithiated m-carborane assisted by a copper(I) / copper(II) system, and section 3.7 covers the abovementioned coupling approach only employing a copper(II) assist system.

3.2 Ullmann Coupling of C,C'-Diiodo-m-Carborane

The reaction mechanism for Ullmann coupling remains largely uncertain, but is popularly hypothesised as involving metallic complex formation of an organohalide species upon an activated metal (copper) platform.[47] The mechanism postulated relies on the electronegative centre of the species undergoing coupling being in close proximity to the halide substituent, to facilitate nucleophilic substitution necessary to form the complex intermediate. Our efforts in this regard involve attempting to achieve coupling of the diiodinated *meta*-carborane by the Ullmann process, relying on the electronegativity of the carborane cluster, rather than an electronegative substituent, to promote the required complex formation. The dihalogenated starting material, C,C'-diiodo-m-carborane (structure [II]), is readily obtained from the dilithiated species, [I], by reaction with iodine, in accordance with the following schematic representation:



[I] [II]

Scheme (1): Formation of m-I-C-$B_{10}H_{10}$-C-I, [II], from m-Li-C-$B_{10}H_{10}$-C-Li, [I], by iodine substitution.

The product, [II], is obtained in a white platelet crystalline form of melting point 77° - 78°C (sealed tube) (lit.[22] mp 74° - 75°C). The compound develops at approximately $R_f \sim 0.8$ on TLC plates (neutral $A\ell_2O_3$/n-hexane) exhibiting the characteristic halo-carborane trend of UV visibility.

The experimental efforts of this work were directed at the coupling of [II] by way of an Ullmann reaction, according to scheme(2) below, to furnish the diiodinated dimeric-*meta* carborane.

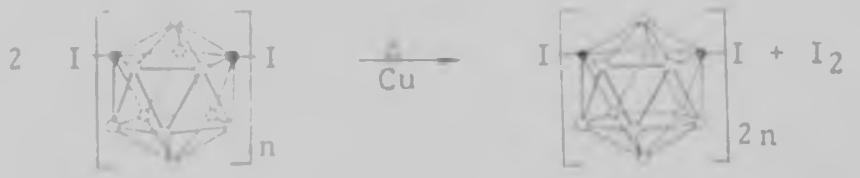
[II] [III]

Scheme(2): Formation of diiodo-bis-*meta*-carborane, [III], by the Ullmann reaction

The reaction conditions involved the addition of activated copper in a 10:1 ratio to [II] at ambient temperatures under strictly controlled anaerobic and moisture free environs. Coupling was then attempted by gradually increasing the temperature to 120°C and permitting the reaction to proceed in the melt for several hours. During this stage, the medium assumed an orange colouration, attributed to liberated iodine.

Chromatographical studies of the reaction products indicated the reaction has not proceeded favourably, exhibiting primarily unreacted starting material and only small amounts of compounds of low R_f values. Separation attempts involved, initially, subdivision of the obtained crude products into categories of hexane-soluble matter (essentially starting material and apparent lower oligomeric materials), following this, the benzene soluble fraction (thought to comprise the higher oligomeric and polymeric compounds) and finally an inorganic fraction as the insolubles. Our efforts focussed on the yellowish compound obtained from hexane extraction which, upon recrystalisation from that solvent, produced essentially the expected starting material, [II]. This was confirmed by melting point data and TLC monitoring. The remaining oils, composed of the lower R_f valued components, because of their limited quantities, were not able to separate further, except in one instance. In this case, the final crystallisation fraction from n-hexane yielded in miniscule quantities an off-white crystalline product of mp 154.0°C - 162.3°C (sealed tube). Examination of this product by TLC (neutral Al_2O_3/n-hexane) indicated the composition of a single substance, at $R_f \sim 0.6$, demonstrating the characteristic ultra-violet visibility of halogenated carborane derivatives, and was thus thought to be the product [III]. Attempts at duplicating these results, however, did not prove fruitful and further investigation of this compound was not possible. Additionally, the small amounts of the dark oil obtained from the benzene extracted portion were not pursued further on account of both the small quantities obtained and time restraints.

The poor performance evident with scheme (2) suggests that a combination of the delocalisation of the charge distribution of the starting materials cluster matrix and the steric effects associated in its complex formation with the copper provides an inappropriate stage for the reaction to proceed. In view of the intent of establishing a basis for dimerisation from which further coupling may be investigated, it could be argued that, in accordance with scheme(3), this method would be severely hampered, in the case of compound [IV], by the effects of conjugation of these super-aromatic constituents both upon the charge distribution and the steric effects of the molecules. In light of the above, this reaction type was abandoned in the pursuit of alternative dimerisation approaches.

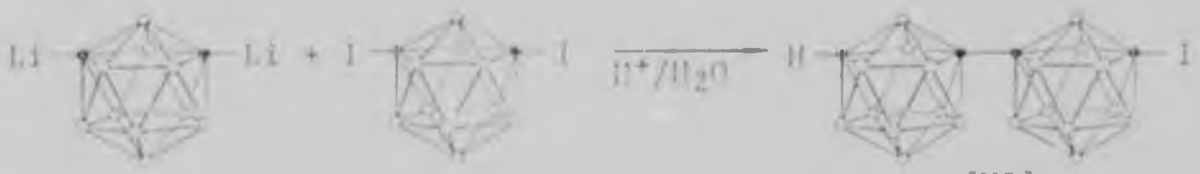


[IV] [V] n ⩾ 2

Scheme(3): Higher oligomeric coupling of idodinated-meta-carborane species by the Ullmann reaction

3.3 Direct Coupling of C,C'-Dilithio-*m*-Carborane with C,C'-Diiodo-*m*-Carborane

The approach assumed in the efforts described in this section comprised the initial coupling attempts of carbon-linked dimeric-*meta*-carborane formation. The materials selected to achieve this goal consisted of the nucleophilic C,C'-dilithio-*m*-carborane (compound [I]) on the one hand and its derivative, C,C'-diiodo-*m*-carborane (compound [II]), on the other, as the electrophilic species. The envisaged reaction process is depicted in the following schematic representation.



[I] [II] [VI]

Scheme(4): Formation of mono-iodo-bi-*meta*-carborane [VI], by direct coupling *via* carborane's ionic transition states.

The success of the abovementioned reaction scheme would provide a desirable and convenient synthetic method for dimerisation of the *meta*-carborane species by virtue of of the relative ease of formation of the starting materials utilised. The reaction type would additionally prove useful in future studies, of potential progression to the higher oligomeric and polymeric structures of directly-linked carborane species, by appropriately altering the reaction conditions. The material choice of employing disubstituted carborane derivates was intended to provide enhanced reaction capabilities for coupling. In the instance of compound [I], the convenience of formation and assured uniformity of the material, over its mono-lithiated counterpart, were additionally considered factors. In the selection of compound [II], the potential of hydrogen abstraction, as would be present with mono-iodo-carborane, was eliminated.

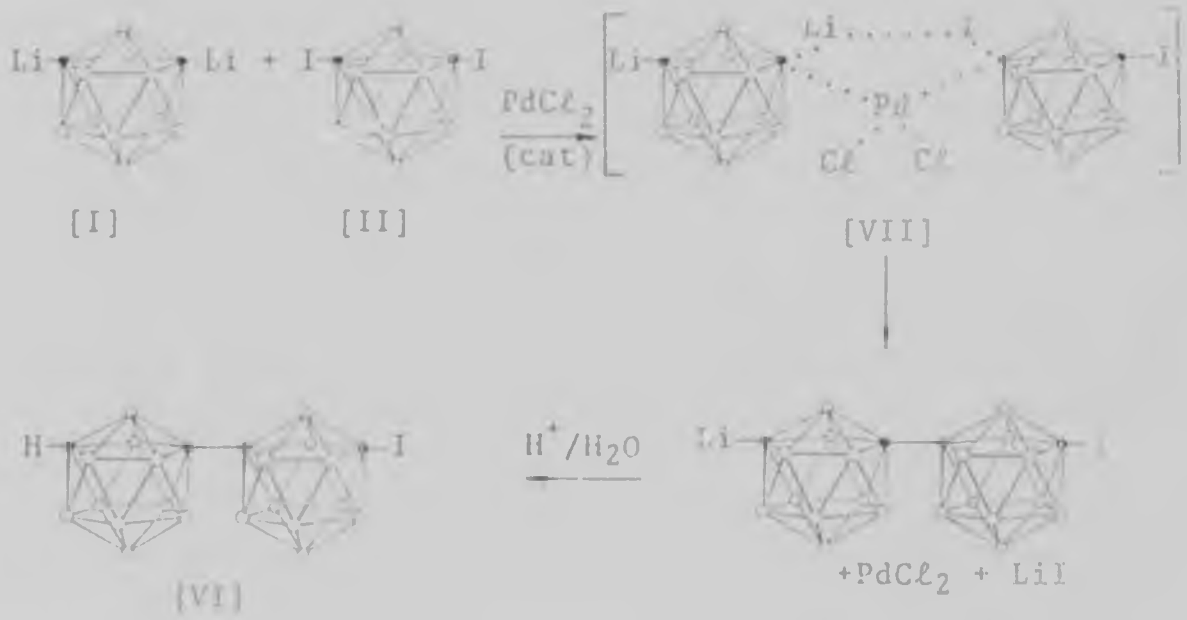
The immediately evident drawbacks, in this unaided approach to synthesising the compound [VI], rest in the starting materials themselves. Formation of substance [II] from [I], as per scheme(1), provides no evidence of coupling. This fact has, however, been attributed to the reaction conditions pertaining to both the solvent medium and temperature. Secondly, the cationic applicability of [II] remains essentially uncertain.

The experimental approach employed in this reaction scheme involved the treatment of [I], obtained by the standard lithiation procedure, with a formal equivalent of [II] in a tetrahydrofuran solvent medium under carefully controlled anaerobic and moisture-free conditions. The crude yellow-orange oil product which was subdivided into hexane and thereafter benzene-soluble portions. Observations made by TLC proved somewhat discouraging, indicating some reaction had occurred, by the presence of several low R_f valued constituents, but these appeared only to have occurred in very minor quantities. Included in our attempts at product separation (hexane-soluble portion) were crystallisation, sublimation, dry-column and liquid chromatographics, all proving unsuccessful. As a final effort in this reaction series, a combined L.C. fraction, appearing to have concentrated those components in the R_f 0.4 region, was subjected to mass spectral evaluation. The results were essentially too complex to analyse fully, attributed to the impure nature of the sample, but did indicate considerable lithium-iodine interchange had occu[illegible] by the presence of mono-iodo-m-carborane (m/e [illegible]). Higher temperature spectral patterns, too, appear[illegible]lex and served us only in that higher oligomeric [illegible]oducts of the reaction, eg. pentameric and tetrameric m-carboranes (m/e *circa* 713 and 570 respect.), (cf. §4.4.3.), were identified. It was deduced from the majority of the remaining peaks that oxidised or degraded product compounds comprised the bulk of the reaction impurities. Evidence of the formation of the desired product [VI] was not forthcoming.

The overall reaction performance, in terms of the low quantities obtained and the levels of purity achieved indicated that further investigation of this unaided direct approach to coupling was not warranted. We hypothesise that these problems appear to lie rooted in the steric and/or ionic characteristics exhibited by the diiodinated m-carborane starting material. Dilithiocarborane, while not over-active, is sensitive to degradation or oxidation

3.4 Coupling of C,C'-Dilithio-m-Carborane with C,C'-Diiodo-m-Carborane Promoted by a Palladium(II) Catalytic System

The efforts of this experimental phase were directed at promotion of dimeric <u>meta</u>-carborane formation from the ionic starting materials C,C'-dilithio-m-carborane and C,C'-diiodo-m-carborane by the catalytic action of palladium. The reaction scheme outlined below depicts the anticipated coupling



Scheme (5): Formation of mono-iodo-bis-<u>meta</u>-carborane, [VI], by palladium(II) catalytic coupling of dilithio-m-carborane, [I], and diiodo-m-carborane, [II].

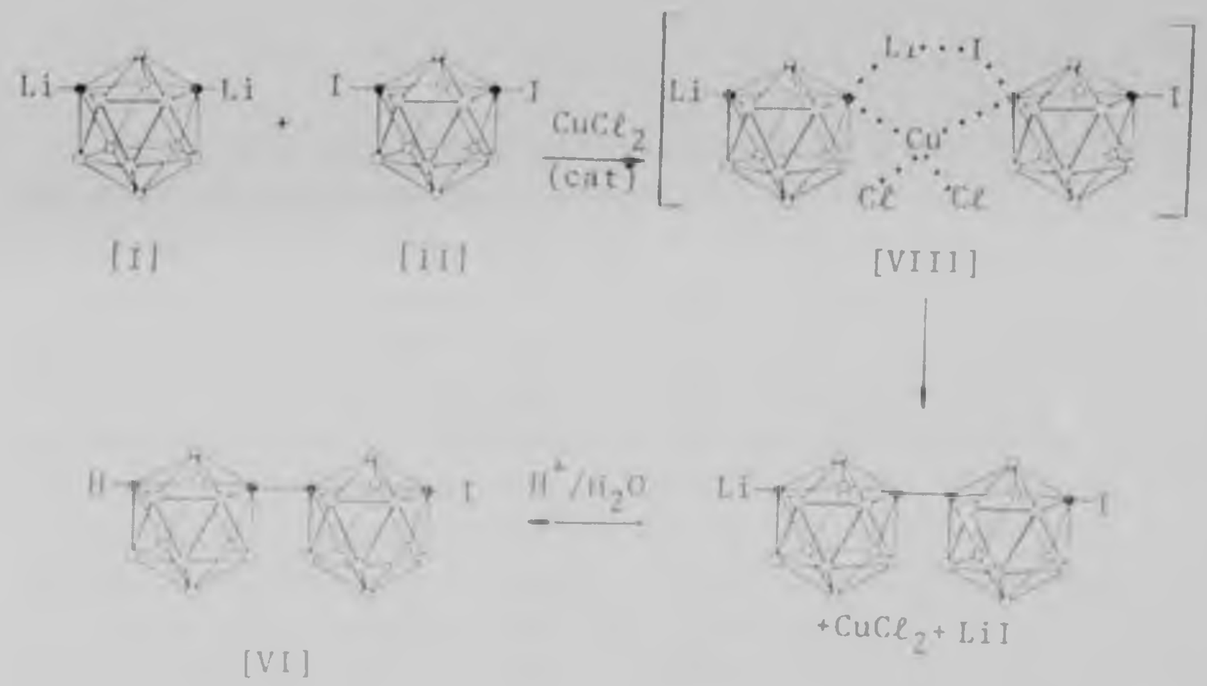
Maintaining the concept of ionic coupling of the m-carborane species, we attempted in these undertakings to achieve coupling by means of a palladium complex intermediate. The exact complex intermediate structure and its mechanism of formation are essentially unknown. The schematic representation of this complex, [VII], is intended primarily as a conceptual possibility. The desired function in the formation of such a complex would be to provide the lithio-species with a functionality rendering it less active, whilst promoting the iodo-compound's reactivity and establishing the scenario for carbon-carbon linkage. The hoped for overall effect would be to provide more suitable ionic mobility and reduced steric hindrance.

The reaction processes involved a somewhat similar technique to that established in § 3.3, in that [I] and [II] were added at low temperatures, -70°C, employing tetrahydrofuran or dimethoxyethane solvent media. The latter was preferred in terms of low temperature viscosities. This proceedure, however, differed from the previously described in that the reactions were conducted, after the addition stage, at ambient temperatures for periods ranging from 5 to 20 hours. In this fashion reduced by-product formation was expected, as were the possibilities of degradation and/or oxidation. The reaction was terminated by hydrolysing at ice-bath temperature, which gave rise to an orange oil constituting the crude product.

Work-up of the obtained product again consisted of sublimation, crystallisation, dry-column and liquid chromatographies, but indications were that the starting materials comprised the bulk of our product. TLC studies also indicated the formation of several low valued R_f components, essentially of similar appearance and quantity to those obtained in the previously described experimental section. Mass spectral studies, of the same band as that previously investigated, i.e., $R_f \sim 0.4$, gave rise to very much the same peak distribution, except in that mono-iodo-trimeric-meta carborane (m/e~553) constituted the highest mass number of identifiable oligomeric carborane type compounds. No evidence existed, as in our previous section, to suggest the desired product, [VI], had been formed, and further investigation into the product composition was abandoned.

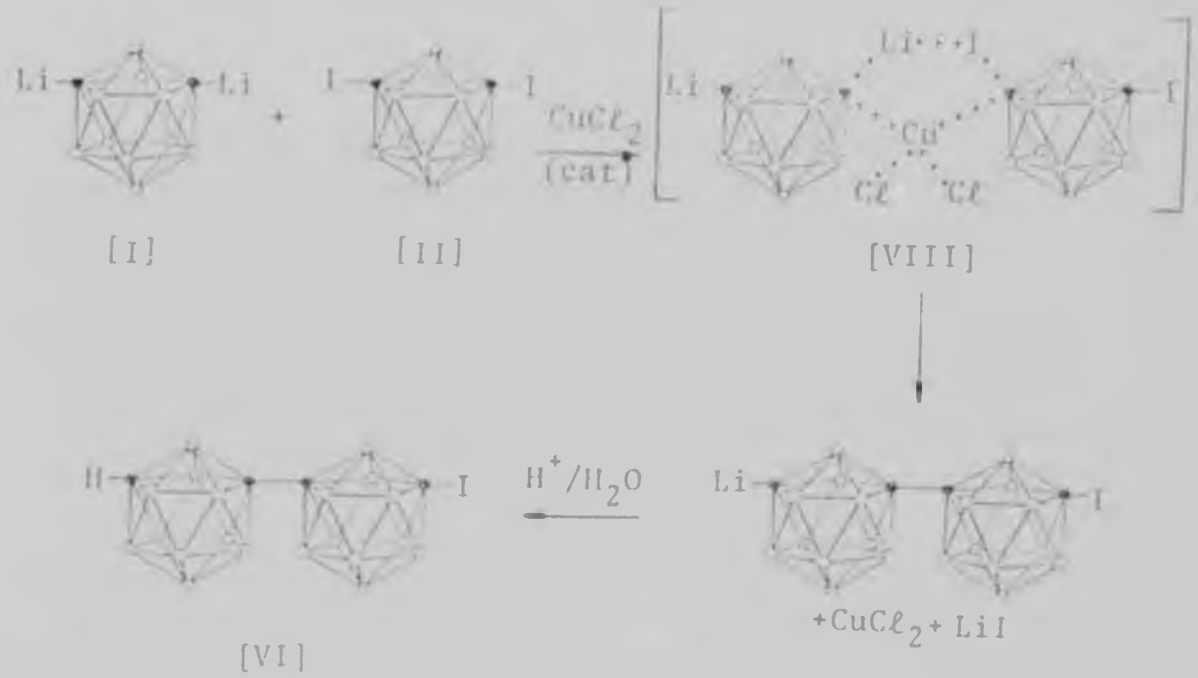
3.5 Coupling of C,C'-Dilithio-m-Carborane with C,C'-Diiodo-m-Carborane Promoted by a Copper(II) Catalytic System

In a final attempt to determine the suitability of the iodinated carborane species in the formation of the dimeric carborane, we embarked upon this experimental phase, maintaining the concept assumed the preceeding section of catalytic coupling of ionic carborane species. The reaction sequence employed, instead of palladium, a copper(II) catalytic system designed to provide a modified complex intermediate structure with improved steric properties over the previously mentioned instance. The schematic representation of this section's approach is outlined in the following;



Scheme (6): Formation of mono-iodo-bis-meta-carborane, [VI], by Copper(II) catalytic coupling of dilithio-m-carborane, [I], and diiodo-m-carborane, [II].

The experimental techniques employed involved the standard lithiation of m-carborane, then the treatment of the product obtained, [I], with stoichiometric amounts of diiodo-m-carborane, [II], and catalytic quantities of cupric chloride at 0°C in a solvent medium of ethylene glycol dimethyl ether. In accordance with standard practices every effort was made to ensure moisture-free and anaerobic conditions, as well as high purity of reagents and solvents. The reaction, after addition, was subjected to a gradual rise in temperature to 65°C and wa maintained thus for two hours before termination at 0°C by acidic hydrolysis.



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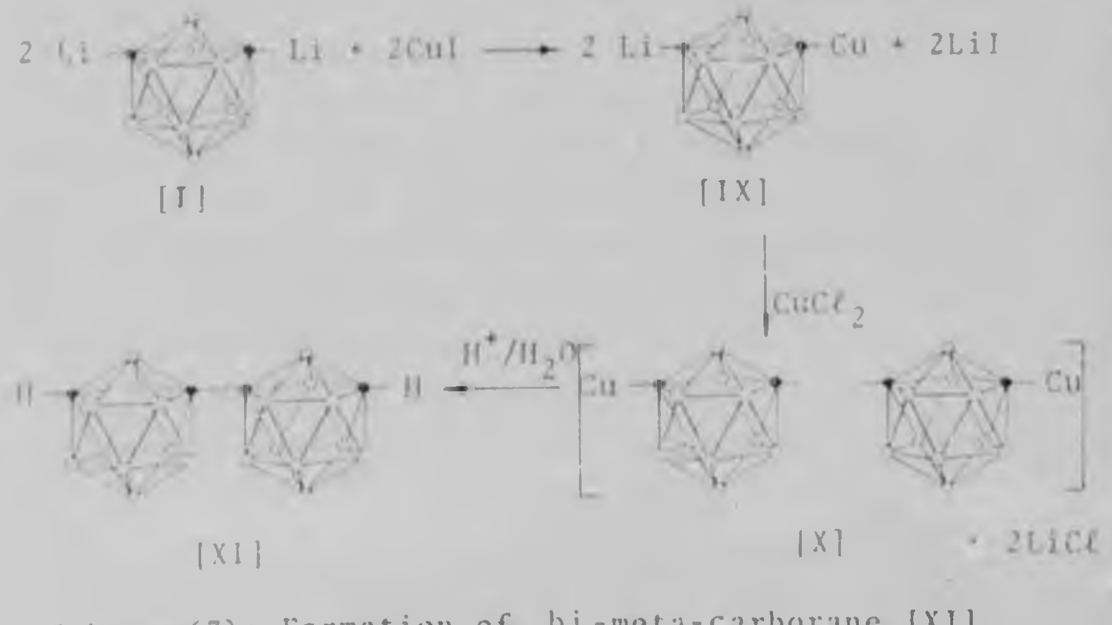
The dark oily compound obtained from the reaction precipitated out a portion of the starting materials upon standing overnight. The remaining crude product was subjected to n-hexane digestion, and separation by means of sublimation and fractional crystallisation was attempted on these hexane-solubles. The sublimed portion consisted of the starting materials, and chromatographical studies indicated the crystallised fractions were composed essentially of starting materials. The remaining reaction products appeared almost identical to those obtained in our previous works in terms of quality and similar in terms of quantity.

We did not embark on pursuing the products of the abovementioned, nor on employing the described ionic coupling system approach further, in achieving the goal of forming dimeric m-carborane. The conclusion reached from our efforts, as outlined to this stage, are that the reactivity of C,C'-diiodo-meta-carborane, compound [II], is the major contributing factor to the poor performance observed in the desired directions. The non-responsive behaviour of this compound we have attributed to, firstly, problems of steric hinderance, stemming from the nature and comparative size of the substituent iodines and, secondly, to altered intra-molecular ionic characteristics of the cluster. By the latter we infer the powerful electronegative behaviour of the carborane's cluster directed at its electron-rich iodo-substituents probably results in C-I bonds that appear predominantly covalent in nature, with very much reduced ionic traits from that expected, and also gives rise to a modified electronic nature of the total cage system.

Although not firmly established, the coupling products that were observed to have formed and were detected in mass spectroscopy studies of the previous sections' undertakings, appeared to be predominantly comprised of carborane building blocks. No evidence of iodine substitution on these products, on the other hand, was observed. The implications of the above are in support of our statement regarding the low reactivity of the iodinated carborane under the conditions employed. In view of this, we turned our attention to the efforts of the following sections where the potential of the lithiated carboranes is examined from the aspects of promotion of auto-coupling.

3.6 Coupling of C,C'-Dilithio-m-Carborane via Copper(I) /Copper(II) Promotion

The approach assumed in this experimental phase, in the search for a suitable dimerisation process for meta-carborane, was aimed at auto-coupling of dilithio m-carborane. Having established the highly reactive nature of the dilithio-compound in our various experimental tasks, we attempted its exploitation *via* the concept of attaining coupling by intermediate metallic complex formation. From the experience gained in our previous efforts with respect to the apparent quantities of coupled species obtained, supposedly from the lithiated m-carborane compound, it was surmised that, for complexing to occur in an efficient manner, catalytic quantities of the metal agent(s) would not suffice. Described in this endeavour, therefore, are our attempts at attaining auto-coupling of C,C'-dilithio-m-carborane promoted by a copper system of the cuprous and cupric forms. The anticipated reaction mechanism of this attempt is outlined in the schematic representation following:



Scheme (7): Formation of bi-meta-carborane, [XI], by copp[illegible] / copper(II) assistance

The reaction involves the treatment of [I], obtained by the standard carborane lithiating procedure, with cuprous iodide in equimolar proportions to form [IX], the organocopper intermediate. The bicarboranyl complex intermediate, represented by structure [X], would, in turn, be obtained by the addition of cupric chloride to [IX]. Bi-meta-carborane would then be obtained from hydrolysis of this complex. The nature of the resultant copper-carbon bonds should facilitate easy removal of the metal during mild acid hydrolysis, generating the dimer [XI].

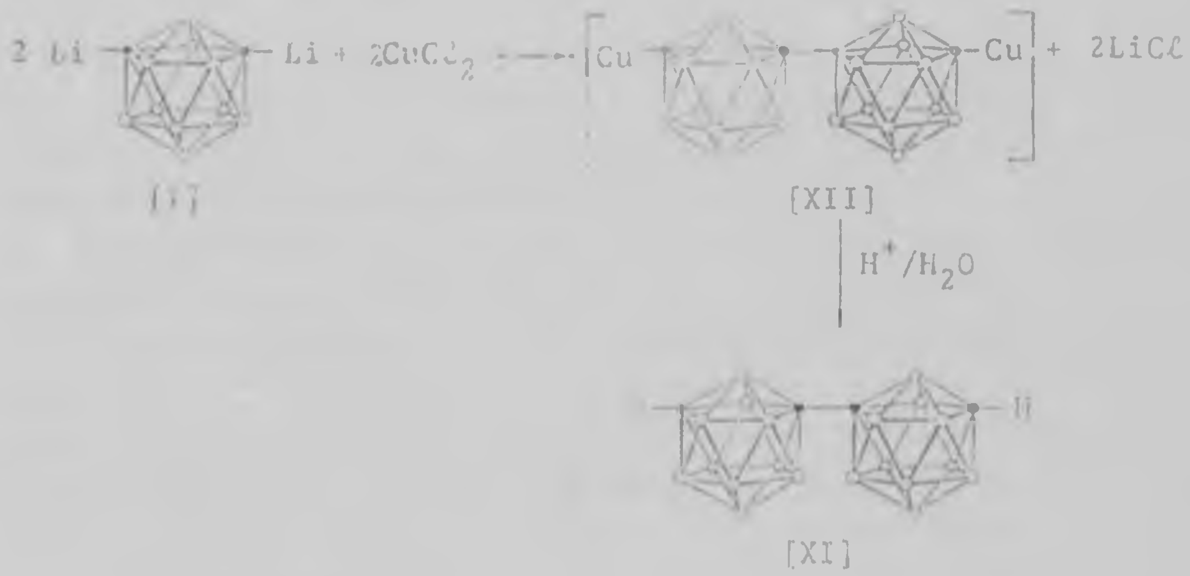
The solvent medium employed in the reaction consisted of diethylene glycol dimethyl ether. (The use of tetrahydrofuran in one of these reactions appeared to give rise to reduced process efficiency.) The addition of cuprous iodide to [I] was attempted at reduced temperature (-70°C) maintaining our standard practice of high-purity solvent and reagent preparation with the exclusion of water and air from all elements of the system. After a 1-2 hour residence time at low temperatures, the reaction mixture was permitted to achieve ambient temperature for approximately 15 minutes, then the temperature was lowered again to -70°C for the second stage of the operation. An excess of cupric chloride was introduced to the reaction and, after a gradual overnight rise to room temperature, the temperature was raised to 50°C for an hour. Hydrolytic reaction termination was performed in the standard fashion.

Investigation by TLC ($A\ell_2O_3$/n-hexane) of the brown organic, soluble reaction product indicated the majority of the product to lie in the starting material band, and a series of products in minor proportions of differing and lower R_f values to form the remainder. The ultra-violet activity of some of these components, including the starting material band, led us to believe iodination of some of the products had probably occurred. Crystalisation attempts of the hexane-soluble product portion, from that solvent, produced essentially *m*-carborane fractions containing compounds of combined R_f values 0.7 to 0.3, and several overlapping lower R_f valued fractions. Mass-spectral studies of one fraction containing the said R_f 0.7 to 0.3 compounds indicated primarily mono-iodo-*m*-carborane (at $m/e \sim 272$), product [XI] (at $m/e \sim 286$), mono-iodinated-bis-*m*-carborane (at approximately m/e of 412), plus various other unidentifiable products to be present. Further crystallisation efforts of the R_f 0.7 to 0.3 fractions from n-hexane did eventually give rise to an isolated TLC spot in the 0.7 region from one crystalline portion. These silvery-white crystals melted at 264 - 267.5°C (sealed tube) and were identified as the sought-after dimer by mixed melting point determinations with the known dimeric compound (refer § 3.7) and with m-carborane (depressed). Additional, but again small, quantities of this product were obtained in another experimental attempt, but no larger portions were obtained either by the abovementioned methods or by liquid chromatography (neutral $A\ell_2O_3$/n-hexane). Similarly, we were not further able to separate the other products observed at low R_f values owing to the quantities involved.

In summary, therefore, the reaction series appeared to give rise to the dimeric m-carborane compound, but in an inefficient manner both from the aspects of quantities and by-product formation. These by-products are largely attributed to side-reactions involving the iodide anion of the cuprous salt, and higher m-carborane oligomers formed. The indications are the cuprous salt is not adequately performing its designed task of tagging the carborane's carbon and, furthermore, the iodine attachment proves problematic with respect to unwanted product formation. As no observed chlorine-containing by-products were obtained, it was surmised the cupric salt did not suffer the same drawbacks, and the next section's efforts were thus focussed on employing this system solely in our coupling arrangements.

3.7 Coupling of C,C'-Dilithio-m-Carborane via Copper(II) Promotion

The series of experiments performed under this section of the work employed one of the simplest, yet most successful, approaches to the dimeric m-carborane. The attempted reactions employed the treatment of the dilithiated derivative of meta-carborane with cupric chloride according to the scheme outlined below:



Scheme (3): Formation of bi-meta-carborane [XI] by copper(II) assistance

This approach to dimerisation is presented as the logical continuation of the aforementioned coupling attempts. In reviewing the previously described attempts we failed to achieve substantial results in the instances of Ullmann coupling, of the reaction of diiodinated-m-carborane with activated copper, as well as in those of the ionic coupling attempts employing diiodinated or dilithiated species either directly or with a catalytic agent. We attempted in this section the formation of a coupled unit by means of metallic-complex intermediates involving only the dilithiated *m*-carborane species. The preceeding efforts successfully utilised copper in oxidation states (I) and (II) with the dilithiated compound to form bi-*m*-carborane. Reaction by-products of an iodinated nature primarily (from the cuprous salt), however, hampered these efforts resulting in the present approach.

The objective established for this reaction series was the formation of a metal bi-*m*-carborane complex intermediate which would result in the formation of [XI] upon removing the metal. As the reaction mechanism has not been firmly established, the complex intermediate's structure is essentially unknown, but, for the sake of convenience, is represented by the structure [XII] in reaction scheme (8). Our efforts did not include isolation/elucidation of this compound owing to time restraints. A concern in this reaction sequence arose from the attachment potential of those carbons not desired to partake in the coupling reactions at this stage and existing in a cuprated form. The dilithiated *m*-carborane species was still desired as a starting material to conform with the aims established of providing an attractive stage for potential future polymeric synthesis and also because it was more conveniently produced than the mono-lithiated species.

Thus, in order to overcome the problem of competing higher order oligomeric reactions, the present approach utilized an excess of the copper salt and mild reaction conditions to control product formation. The role of those carbon atoms not employed in the coupling process is uncertain, but in all probability the carbons are responsible for the formation of an intermediate complex structure with the excess metal present and thereby provide a block against further reaction. The apparent success of this approach negated an alternative approach of reverting to the mono-lithiated m-carborane derivative in attaining the dimeric product.

The initial experiments involved direct addition of the anhydrous cupric salt to [I] at -70°C, without removal of the spent lithiating solution consisting of diethyl ether as solvent and unreacted butyl-lithium (originally 15% in n-hexane). The treatment following the addition involved a gradual rise in temperature to the ambient, at which it remained 24 hours. Ensuring anaerobic and moisture free conditions, prepurified tetrahydrofuran was introduced as the coupling solvent. The temperature of the process was gradually raised to approximately 60°C, the etherial portion was distilled off in the process, and the reaction temperature was maintained at 60°C for typically four hours. Permitted to achieve ambient temperature overnight, the reaction mixture was cooled further to 0°C, where termination was affected by hydrolysing to a mildly acidic solution by the standard procedure. The green solid product obtained was digested in n-hexane to remove the portion of interest. The remainder, treated with boiling benzene, yielded trace amounts of dark oily substance, assumed to be high oligomers and polymeric by-products of the reaction.

Preliminary identification of the hexane soluble product fraction was performed by TLC (neutral $A\ell_2O_3$, n-hexane mobile phase) indicating the presence of two primary compounds at $R_f \sim 0.8$ (taken to be m-carborane) and the other at $R_f \sim 0.7$. Treatment of this product involved a sublimation (70°C/4 mm Hg) to remove the bulk of the unreacted m-carborane and several crystallisation attempts from n-hexane. In this fashion the product observed at $R_f \sim 0.7$ was obtained in sizeable yields in a very pure form. Its characteristic melting point was 271.0° - 272.2°C (sealed tube/Ar) which underwent a depression when mixed with m-carborane. Our expectations of having successfully synthesised the dimer [XI] were confirmed by mass-spectroscopic and infra-red studies.

Mass spectroscopy gave rise to a major peak distribution for this compound around m/e of 285 and a minor peak distribution in the m/e 141 region. Both peaks exhibited the characteristic profiles of the carboranes as depicted in figures 4 and 5. Infra-red spectroscopy of this compound resulted in similar absorptions to that for m-carborane, differing slightly in some areas as evident from the attached figures 6 and 7. The distinctive characteristic feature of this compound appeared in the form of a split breathing mode at 720 cm^{-1}. Furthermore, the C-H stretching band was found shifted to 3020 cm^{-1} in m-carborane, and the C-H bending peak exhibited at 1160 cm^{-1} by m-carborane appeared at 1130 cm^{-1} in the spectrum of (XI). The remaining peaks, B-H stretching at 2590 cm^{-1} and the three fingerprint-region peaks at 1080, 1040 and 1000 cm^{-1}, were essentially unaltered.

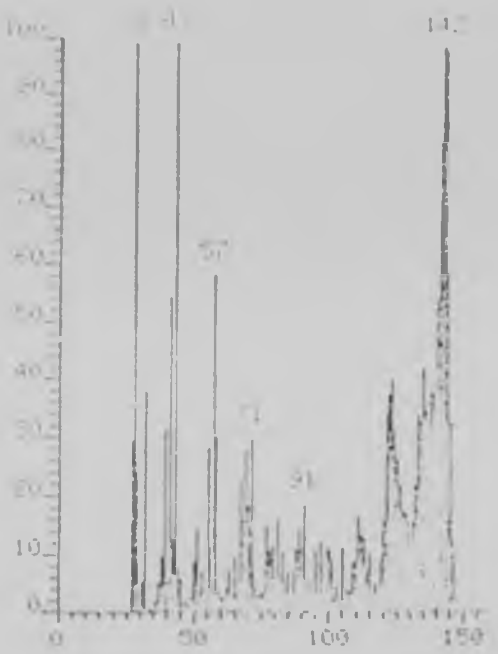


Figure 4 : Mass Spectrum Of m-Carborane

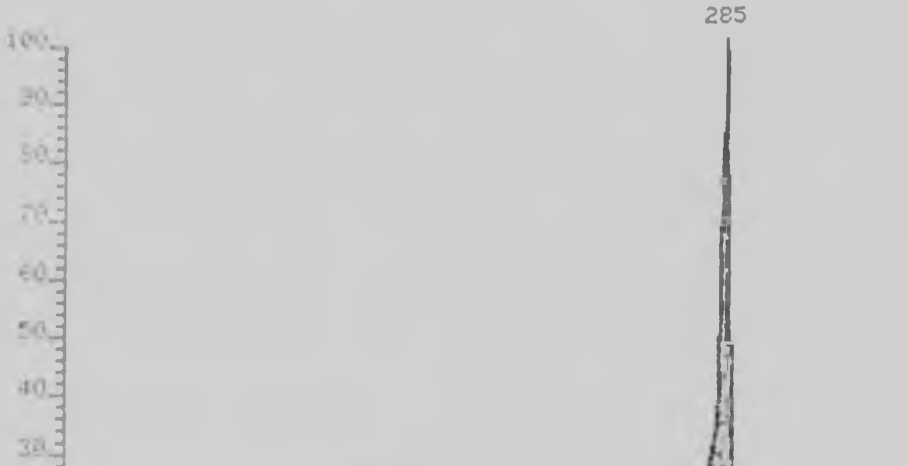


Figure 5 : Mass Spectrum Of Bi-m-Carborane

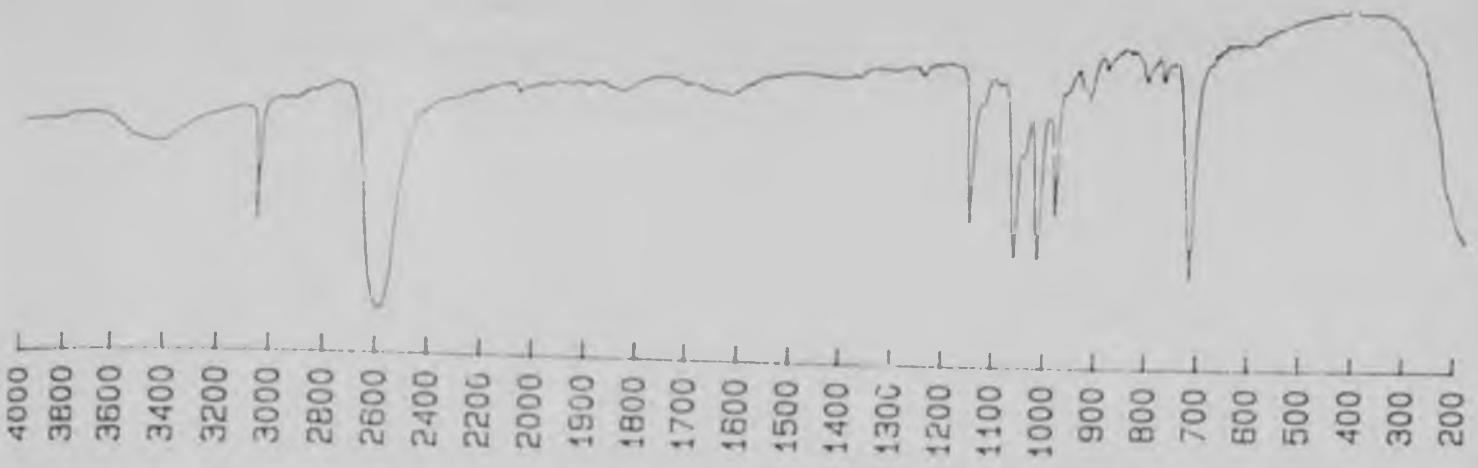


Figure 6 : Infra-red Spectrum Of m-Carborane

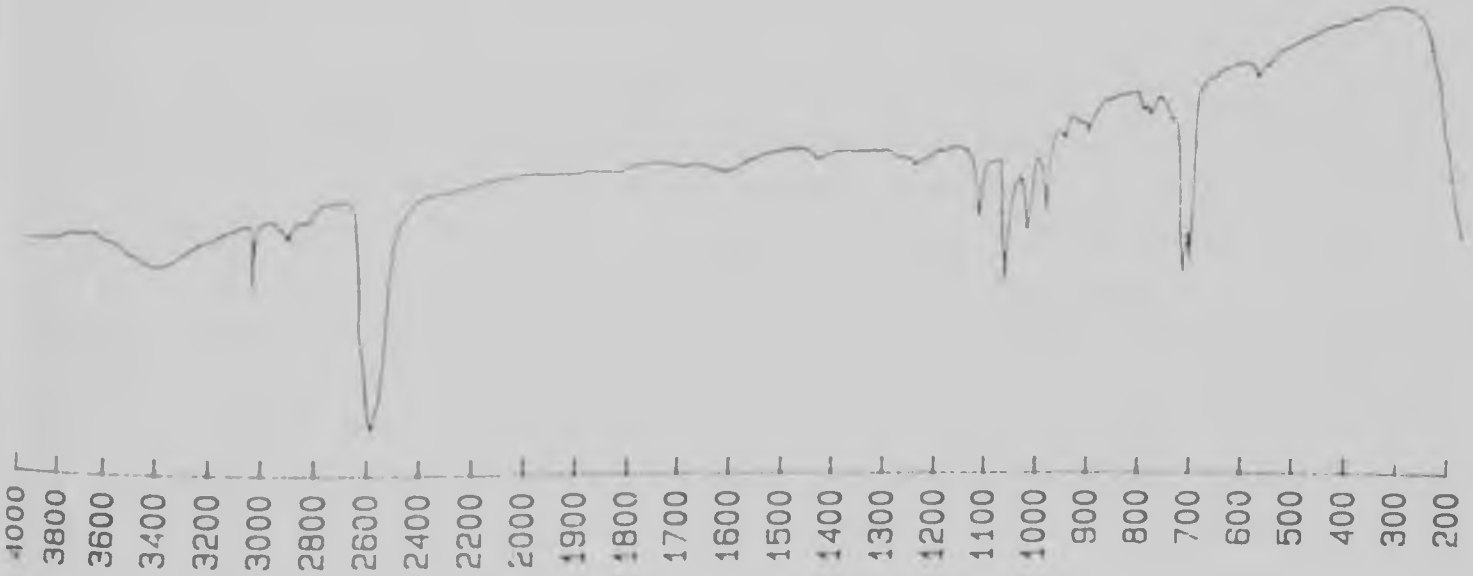


Figure 7 : Infra-red Spectrum Of Bi-m-Carborane

Figure 6 : Infra-red Spectrum Of m-Carborane

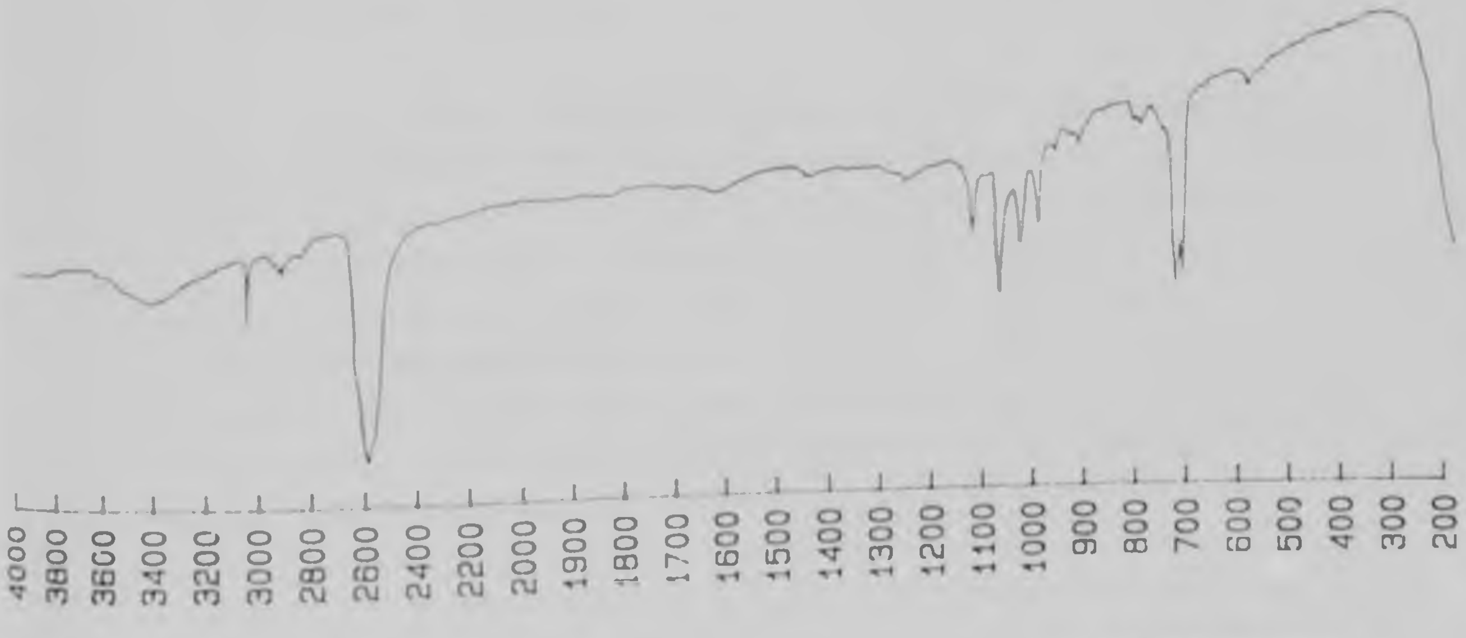


Figure 7 : Infra-red Spectrum Of Bi-m-Carborane

An alternative approach to this product, employed in some of the later reaction sequences, attempted the coupling of the starting material,[I], in its solid state, by the addition of cupric chloride in a diethyl-ether: benzene (15:1) medium at -70°C. After being permitted to gradually achieve room temperature, the reaction mixture was refluxed for 10 minutes and terminated in the standard fashion. The starting material was obtained in its solid form by conducting the lithiation reaction in a n-hexane: diethyl-ether (1:1)solvent medium, separating the solid lithiated product from the mother-liquor and washing with n-hexane. This method, however, proved less efficient than the former both in terms of yields and contaminated products.

A further attempt at promoting carborane coupling was conducted by the introduction of oxygen into the system. [I], obtained in the above-described manner, was taken up in diethylene glycol dimethyl ether for the addition of the anhydrous copper salt at -70°C. The copper addition was performed in two stages in these instances, both at low temperatures and interspaced by a brief (approx. 5 minute) period at room temperature. After adding the second half of the copper salt and maintaining -70°C for 2 hours, oxygen was bubbled through the reaction solution for 20 minutes. During this time, the solution changed from a dark green colouration to red. Allowing the temperature gradually to achieve room temperature overnight, the reaction was completed by heating at 50°C for an hour and hydrolysed at 0°C with acidified degassed water. The crude product obtained in this fashion appeared from TLC to contain numerous by-products, of low R_f values, resulting in poor yields of the desired product [XI]. The TLC studies intimated the reaction by products to consist of high oligomers of carborane as well as some alcoholic or acidic derivatives, from the white appearance of the TLC plates under both ultra-violet and iodine developments. Of these, mono-hydroxy-*m*-carborane was separated, its structure confirmed by mass-spectral studies -refer figure 8 . Additionally, evidence of mono-hydroxy-bi-*m*-carborane (m/e ~ 302 region) was observed in an impure product sample mix. Owing to the low yields obtained and interference of the contaminants, [XI] was not successfully isolated.

The first-mentioned coupling reaction, employing [I] in its mother-liquor together with cupric chloride, appeared to give rise to optimum reaction yields within the scope of this section. Upon the basis of pure and isolated bis-*m*-carborane,[XI],converted from *m*-carborane starting material, indicated at least 30% yield had occurred. Other products of the reaction were, asides from unreacted starting materials, some higher oligomeric forms (based upon observation of trimeric-*m*-carborane impurity in one mass spectral study and corresponding TLC observations) and very small amounts of supposed polymeric material (precipitated from the benzene soluble fractions upon addition of n-hexane). No attempts were made at investigating these compounds further due to the small quantities obtained and time restraints. In those instances of the alternative approach of employing the separated starting from TLC to contain numerous by-products, of low R_f values, resulting in poor yields of the desired product [XI]. The TLC studies intimated the reaction by-products to consist of high oligomers of carborane as well as some alcoholic or acidic derivatives, from the white appearance of the TLC plates under both ultra-violet and iodine developments. Of these, mono-hydroxy-m-carborane was separated, its structure confirmed by mass-spectral studies -refer figure 8. Additionally, evidence of mono-hydroxy-bi-m-carborane (m/e ~ 302 region) was observed in an impure product sample mix. Owing to the low yields obtained and interference of the contaminants, [XI] was not successfully isolated.

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In summary of this chapter's undertakings, we conclude that a fairly attractive yield of the desired bis-*m*-carborane, [XI], may be achieved by treatment of the lithiated species of *m*-carborane with copper(II) chloride. Optimum conditions involve employing the lithiated product without prior removal of the lithiating solution, conducting complex formation with copper(II), and subsequent dimerisation by mild heating in a tetrahydrofuran medium.

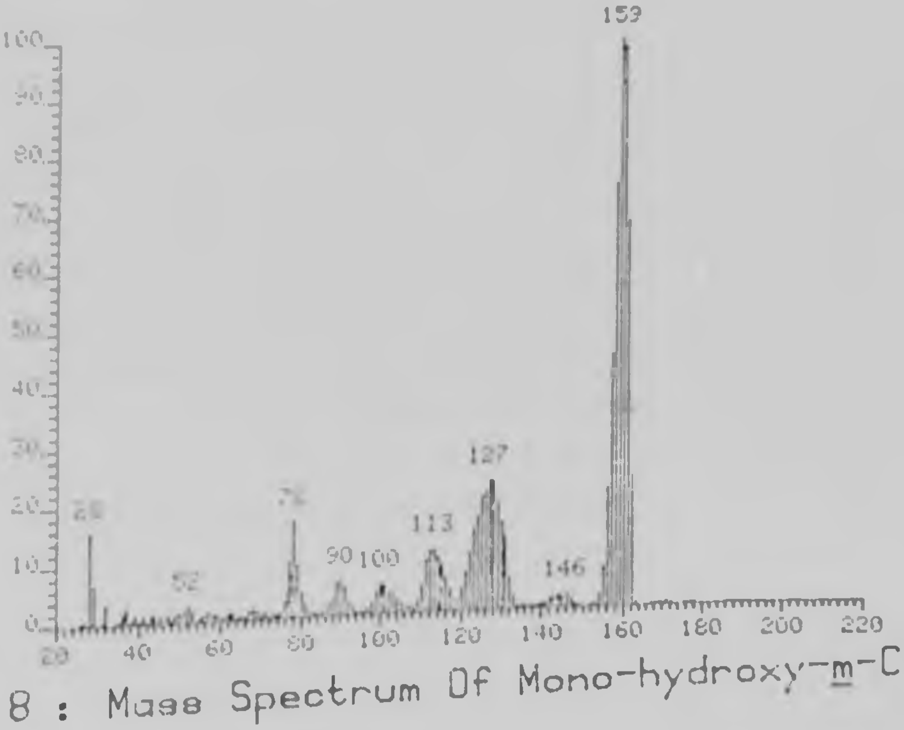

Figure 8 : Mass Spectrum Of Mono-hydroxy-*m*-Carborane

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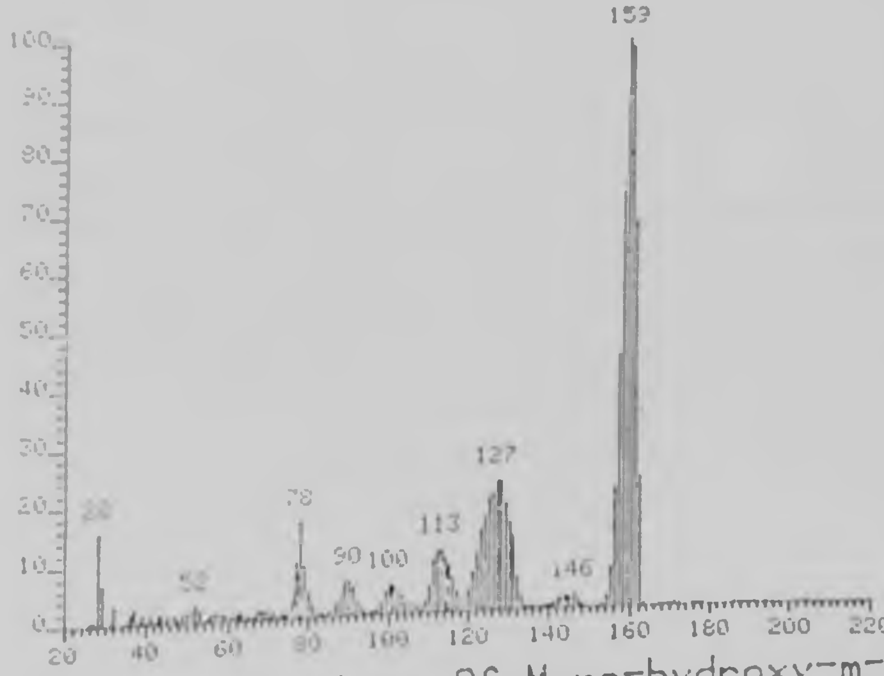

Figure 8 : Mass Spectrum Of Mono-hydroxy-m-Carborane

4. EXPERIMENTAL

4.1 Instrumental Methods, Analysis Procedures and Apparatus

Mass spectroscopy was performed on a Varian Mat-312 Mass Spectrophotometer in conjunction with the Varian SS-188 data systems as well as a Varian Mat CH-5 system. Infra-red spectroscopy was performed on a Perkin Elmer 521 Spectometer (4000 - 200 cm^{-1}) employing primarily KBr discs for both solid and liquid film compounds. Melting point determinations were performed in sealed tubes under argon and were measured up to 350°C.

Thin layer chromatography employed neutral-grade aluminum oxide plates (supplier: Merck). Development was conducted both by ultra-violet light and iodine vapours. Liquid chromatography employed neutral alumina, grade I (Merck). The columns were dry-packed and degassed for a minimum of eighteen hours prior to use with dry argon. Dry-column chromatography employed Woelm dry-column grade alumina, neutral, in 2 cm diameter columns, degassed for a minimum of eighteen hours with dry argon. Sublimation was performed in water-cooled sublimators under reduced pressure (3-4 torr). Samples were dried in a jacket-heated desiccator at 3-4 torr over P_2O_5.

The apparatus employed for lithiation and some subsequent experimentation employing the lithiated product was constructed as demonstrated in figure 9.[66] All apparatus was baked for 18 hours at 130°C, assembled while still hot, flooded with dry argon while cooling and flamed three times, maintaining a positive flow of argon, prior to the reaction.

4.2 Solvents and Reagents

Pretreatment of major solvents and reagents for use in our reactions was performed as follows:

4.2.1 n-Hexane

The solvent was shaken successively with small portions of conc. H_2SO_4 until the acid portion remaining was colourless. Solvent then washed successively with water, aq. 10% Na_2CO_3, water (twice), and dried with $MgSO_4$. The hexane was distilled from sodium wire in predried and deaerated apparatus with argon bubbled through the solution. The distillate was collected and stored over sodium wire.[39]

4.2.2 Diethyl Ether

The ether was shaken with 1% of its volume of a solution of ferrous sulphate and conc. H_2SO_4 in water (6 ml of conc. H_2SO_4 with 6.0g of ferrous sulphate in 110 ml of water typically). The ether was washed with water and dried for 24 hours with $CaCl_2$, filtered and dried over sodium wire until the sodium remained bright. Distillation from sodium was conducted just prior to use in predried, deaerated apparatus with dried argon passing through the system.[39]

4.2.3 Tetrahydrofuran

The solvent was refluxed with and distilled from $LiA\ell H_4$, dried over sodium, from which it was fractionally distilled (predried, dearated apparatus with argon bubbled through) and stored over CaH_2.[39]

4.2.4 Benzene

The benzene was shaken with conc. H_2SO_4 until free from thiophene, then water, dil. NaOH and water, followed by drying over CaH_2. The solvent was then distilled (predried deaerated apparatus with dry argon bubbled through the solution) and stored over CaH_2.[39]

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4.2.5 Dimethoxyethane (Ethylene glycol dimethyl Ether)

The solvent was refluxed under a steady stream of argon over sodium, decanted into predried deaerated distillation apparatus, maintaining the argon stream, and distilled from sodium, and stored over that metal.[39]

4.2.6 Diethylene Glycol Dimethyl Ether

The solvent, diglyme, was predried and refluxed over CaH_2; it was then distilled from sodium under reduced pressure in an argon stream. Storage over sodium wire.[39]

4.2.7 Hydrolysis Solution

Distilled water was boiled and a rapid stream of argon bubbled through while cooling; $HC\ell$ was added to make a 2.5% v/v solution.[66]

4.2.8 Activated Copper-Bronze

10g of copper bronze (source Schuchardt Munchen) was treated with 100 ml of a 2% iodine in acetone solution for 5-10 minutes. The product was filtered under vacuum, removed and washed with 50 ml of a 1:1 conc. $HC\ell$: acetone solution. The product was dried in a vacuum desiccator and used immediately after drying.[65]

4.2.9 Copper(II) Chloride

$CuCl_2 \cdot 2H_2O$ was heated overnight at 120°C under high vacuum with P_2O_5 desicant, then flushed with dry argon and cooled under a mild positive pressure of that gas.

4.2.10 Copper(I) Iodide

Potassium iodide, 0.55 mol, in 150 ml of water was added to 0.25 mol of copper sulphate (hydrated) in 250 ml of water with stirring for 30 min. CuI was allowed to precipitate overnight and was filtered. The product was washed with a 5% KI solution and dried over P_2O_5 under high vacuum at 80°C. Finally, it was cooled to ambient temperature under argon.

4.3 Starting Material Preparation

4.3.1 m-Carborane

The crude compound, supplied by Olin, was purified by crystallisation from hot toluene, followed by sublimation at typically 50° - 70°C under high vacuum. Immediately prior to use the m-carborane, contained in predried and deaerated apparatus, was again subjected to vacuum, flamed briefly and flooded with dry argon. The latter procedure was repeated 3 times.

4.3.2 C,C'-dilithio-m-carborane

Alternative [A] (typical reaction) - m-Carborane, 0.056 mol, treated as in 4.3.1, was added to the 1-litre four-necked round-bottom flask (item (1) in figure 9) *via* a 100-ml round-bottom flask(6) with spout adaptor(5). To the vessel was added 200 ml precooled diethyl ether from funnel(4). (During such stages, the gas outlet vent(2) was seated in the top of the funnel). The reagents were cooled to -10°C, approximately, in an ice/salt bath(10). Precooled butyllithium (1.9M), 0.120 mol, was pipetted(8) (employing special bottle adaptor(9)) into 100 ml of precooled diethyl ether in a fresh flash(1). The butyllithium solution was added to the stirred m-carborane solution dropwise over a 20-minute period, the temperature maintained at -10°C for an additional 30 minutes and the reaction was then permitted to run at room temperature for 2 hours. The resultant solution was employed as such for further work. (It was determined from the unreacted m-carborane in the n-hexane washings of an evaporated lithiation solution that approximately 90% conversion can be expected from this procedure).

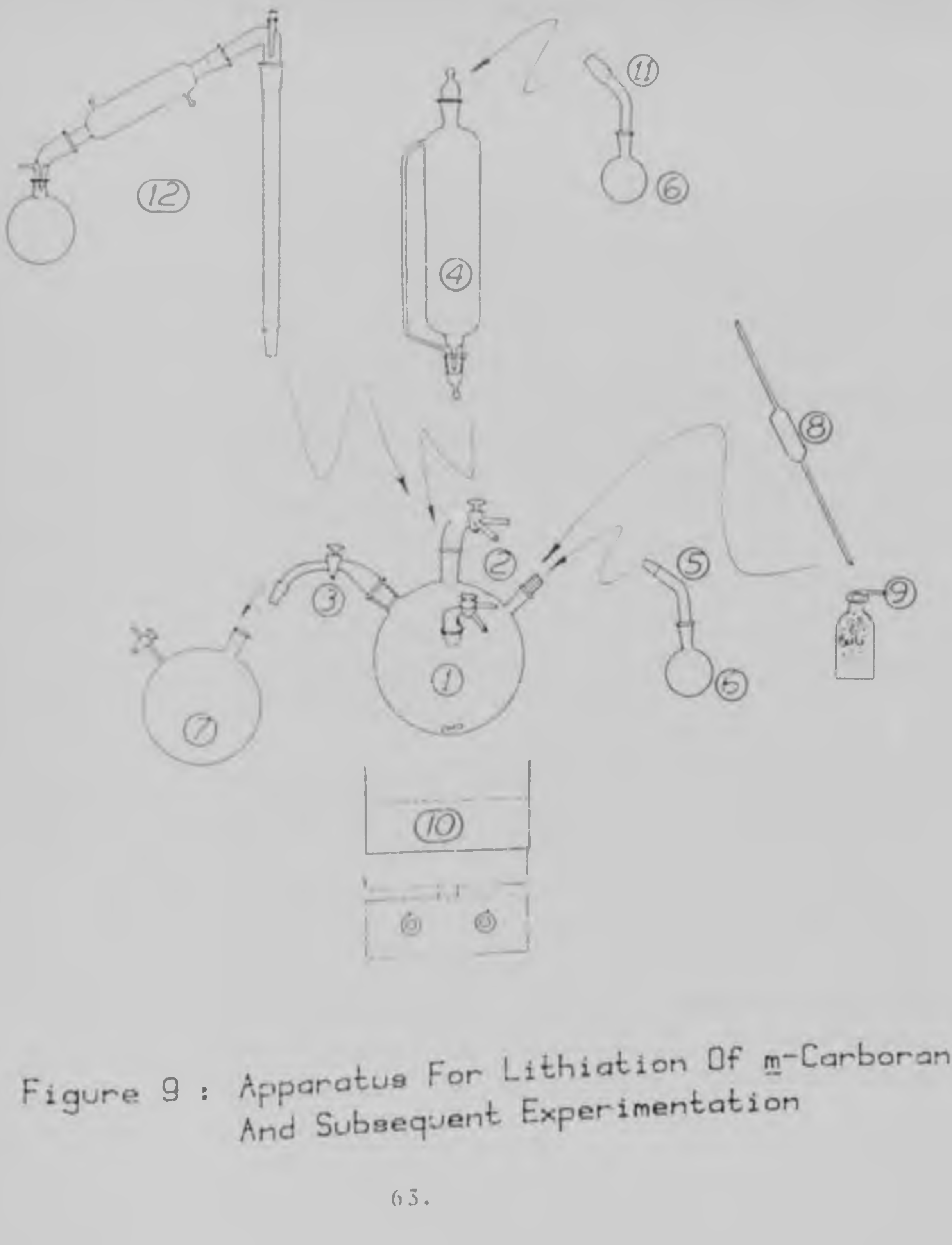

Figure 9 : Apparatus For Lithiation Of m-Carborane And Subsequent Experimentation

Alternative [B] - The identical system to the previously described one was employed in forming the dilithiated m-carborane product, except n-hexane replaced diethyl ether as the solvent.

Alternative [C] (typical reaction) - By altering the solvent solution of the previous reaction procedure to diethyl ether: n-hexane (1:1), solid dilithiated m-carborane precipitated from the solution. The spent liquor was decanted off and filtered through adaptor(3) (fitted with fine glass frit) into flask(7) by pressure differentials. The lithiated product was washed several times with 150 ml portions of n-hexane. The spent liquor together with the washings yielded upon hydrolysis, separation and evaporation, the unreacted m-carborane, typically indicating a 9[illegible]nversion had occurred in lithiation.

4.3.3 C,C'-diiodo-m-carborane: (typical reaction) - To the reaction solution of 4.3.2, alternative [A], at -70°C, was added 0.122 mol of iodine (preflamed under vacuum and flooded with dry argon 4 times) dissolved in 100 ml of precooled diethyl ether dropwise over a 15 minute period from fresh funnel(4) (Iodine added to ether *via* fresh flask 6 and adaptor(11)). The reaction was run at -70°C for a further 30 minutes, then at 0°C for 60 minutes and room temperature thereafter for 60 minutes. Hydrolysis, separation and evaporation of the organic phase yielded an orange oil. The crude product dissolved in warm ethanol (or methanol) was treated with water, until the solution just began turning cloudy, and precipitated out white or yellow white crystals, mp 72.0° - 73.6°C typically. Recrystalisation by this method yielded white platelets of diiodo m-carborane, typical mp 78.8° - 79.1°C, in a 60% yield from m-carborane. (Drying was performed under high vacuum over P_2O_5 at 40°C.)

Found: C : 6 42, H : 2.50

Calculated C : 6.066, H : 2.545

Alternative reaction: (typical procedure) - Employing reaction solution of 4.3.2, alternative [B], was performed by essentially the same procedure as previously discribed, except in that the iodine solution was added to the suspension of the lithiated product in 150 ml diethyl ether.

The diiodo-m-carborane was stored over P_2O_5 and, immediately prior to use, was flamed under vacuum and flooded with argon 4 times.

4.4 Reaction Procedures

4.4.1 General

The reaction procedures outlined are typical of the experiments discussed under section 3 and follow the sequence outlined in that section. Anaerobic and moisture-free conditions were maintained throughout the experimental phases by previously indicated fashions.

4.4.2 Ullmann coupling attempt of C,C'-diiodo-*m*-carborane: 0.050 mol of activated copper together with 0.0025 mol of diiodo-*m*-carborane were added together in a 50-ml round-bottomed flask and a rapid stream of argon passed over them for 30 minutes. Thereafter the temperature was raised to 120°C in several increments (85°C for 1 hour, 45°C for 7 hours, 115° for 7 hours) and maintained thus for 7 hours. Sublimation at 30°C overnight and 60°C for 8 hours under vacuum (4 torr) separated only trace amounts of starting material. n-Hexane digestion of the crude product remaining yielded 0.712 g of a yellow compound. Subjecting this to n-hexane recrystallisation yielded 0.139 g of off-white crystals (mp 159.0° - 162.3°C) differing from other fractions on TLC only in so far as a base spot (R_f: 0) was observed.

The remaining hexane-solubles existed as a dark oily substance refusing to crystallise further. The n-hexane insoluble portion was digested in benzene yielding 0.014 g of an orange crystaline matter and leaving 2.943 g of insoluble matter.

4.4.3 Direct coupling attempt of C,C'-dilithio- and C,C'-diiodo-m-carborane:

To a lithiated solution of m-carborane, 0.021 mol, at -70°C in a total of 250 ml of n-hexane (vessel(1) of figure 9) was added, over a period of an hour, a 0.021 mol solution of diiodo-m-carborane in 250 ml of precooled tetrahydrofuran. The addition was accompanied by a colour change, from clear, to a milky white liquor. After 30 minutes at -70°C the reaction was permitted to run overnight, achieving room temperature in the process. Heating at 60°C was conducted for 3 hours giving rise to a yellow solution with a white solid suspension. Hydrolysis, washing, drying and evaporation yielded a yellow-orange oil from the organic phase.

The hexane-soluble portion of the oil precipitated, from that solvent, three dark oil fractions (0.199 g total) with the remainder of the same appearance upon running the liquor to dryness. TLC (n-hexane) indicated all these fractions to be essentially similar in composition, with concentration of products in the starting material band vicinity, $R_f \sim 0.8$, and a smaller portion in the $R_f \sim 0.4$ region (developed under both ultra-violet light and iodine exposure). Separation of the remaining oil portion was attempted by crystalisation from n-hexane, giving rise to two fractions in the starting material band (0.478 g total) and the dark oil (2.552 g) remaining after sublimation, was eluted through a 25 cm dry-column with n-hexane. The column cut in approximately 2 cm portions appeared, from TLC to concentrate those lower R_f valued products in the final two fractions. Total 0.204 g.

Additional attempts at isolating the $R_f \sim 0.4$ band involved crystallisation from hexane and ethanol , of dry-column fractions, and liquid chromatography (n-hexane) of combined fractions of the initially precipitated oils from the crude product and the latter mentioned fractions (0.394 g total). Column dimensions were 12 cm x 2 cm employing n-hexane: benzene (75 : 25) eluent, and fractions were collected in 25-ml portions. The final four fractions employed benzene eluent alone. Of the sixteen (oil) fractions collected the fourth to the fifteenth inclusive appeared to be predominantly composed of the products at $R_f \sim 0.4$

(appearance of a double spot on TLC). These combined fractions were submitted for mass spectral evaluation, with results given in Table I. (For the sake of clarity, only that mass number of the predominant line in any particular peak distribution is quoted. The number of lines on either side are recorded in parenthesis, positive for greater mass number and *vica versa*.)

4.4.4 Coupling attempt of C,C' dilithio- and C,C'-diiodo-*m*-carborane promoted by a palladium(II) catalyst:

Separated and washed lithiated *m*-carborane, 0.005 mol, was taken up in 150 ml of tetrahydrofuran-dimethoxyethane (1:1) (vessel(1) figure 9) and cooled to approximately -70°C. To the solution was slowly added, with stirring, 0.006 mol diiodo-*m*-carborane together with 0.003 mmol of palladium chloride in 100 ml of tetrahydrofuran: dimethyoxyethane (1:1). After 2 hours at this temperature the reaction was permitted to run at room temperature for 20 hours. (Colour change over addition period from milky white to a yellow solution). The reaction, after hydrolysis, washing, drying and evaporation, yielded a whitish solid material in an orange oil. Total crude product mass was 2.607 g.

TABLE I: Mass spectrum of products obtained from direct coupling of diiodo- and dilithio-carboranes

Room Temperature

Mass No.		Relative Intensity(%)
522	(+2,-2)	6.9
396	(+2,-2)	16.5
340	(+2,-3)	73.1
326	(+1,-1)	7.7
308	(+5,-5)	21.5
298	(+2,-4)	32.7
289	(0)	9.2
269	(+2,-7)	35.4
223	(0)	7.7
213	(+2,-7)	16.5
205	(0)	7.7
195	(+5,-4)	13.5
180	(+7,-6)	61.5
171	(+2,-11)	57.7
153	(+6,-6)	55.4
149	(0)	69.2
141	(+4,-9)	100.0
135	(+6,-5)	56.2

@ 116 °C

Mass No.		Relative Intensity
713	(+1,-1)	5.2
702	(+2,-2)	6.7
690	(+4,-4)	27.8
664	(+2,-2)	9.4
619	(+1,-1)	7.2
589	(+1,-2)	8.3
576	(+3,-3)	21.1
563	(+5,-6)	100.0
538	(+2,-3)	16.7
446	(+6,-3)	11.1
436	(+6,-13)	69.4
405	(+8,-3)	10.6
340	(+3,-6)	15.6
307	(+16,-14)	51.7

[Values in parenthesis denote no. of lines on each side of quoted major line]

High-vacuum filtration of the crude product gave 0.337 g of solid material containing essentially starting material and minor amounts of compounds in the $R_f \sim 0.4$ (TLC/n-hexane) region. Crystallisation was attempted with this material, but failed to demonstrate any component separation in the three crystal fractions (typical mp 200.8^{o} - 237.0^{o}C).

The oil filtered off the crude product was subjected to sublimation at 57^{o}C, resulting in 0.196 g of yellow solid, identified by TLC as starting material. The oil remaining was digested in n-hexane (giving 0.019 g of insoluble matter) and, failing to crystallise from this liquor, was run to dryness and taken up in hot ethanol. 0.035 g of light brown oily product precipitated from this solution, the composition of which appeared identical to that of the crude product. The remaining oil was finally eluted through an 11 cm x 2 cm alumina column and 25-ml eluent portions (typically) were collected. The mobile phase initially employed was n-hexane, altered to n-hexane: benzene (4:1) at the halfway point, and final extraction was performed with benzene. In this manner, thirty-six fractions were obtained, with starting materials evident in the hexane eluted portions, the compounds (at $R_f \sim 0.4$) becoming evident in the hexane: benzene fractions and appearing to comprise the bulk of the last fraction extracted with benzene - 0.158 g of orange oil. The mass-spectral results of this compound are presented in Table II.

TABLE II: Mass spectrum of products obtained by palladium-catalyzed promotion of diiodo- and dilithio- carborane coupling

Room Temperature

Mass No.	Relative Intensity %
340 (+2,-3)	48.9
323 (+2,-4)	7.1
307 (+7,-4)	21.3
297 (+3,-4)	44.9
282 (+2,-4)	6.2
268 (+3,-6)	28.9
212 (+2,-4)	10.7
197 (+3,-6)	26.7
181 (+8,-7)	62.2
171 (+2,-11)	64.4
153 (+6,-7)	48.4
141 (+4,-10)	100.0
125 (+5,-5)	62.2
113 (+6,-5)	33.3
104 (+3,-7)	40.9

@ 120°C

Mass No.	Relative Intensity %
544 (+1,-1)	6.5
392 (+1,-2)	17.2
374 (+2,-5)	39.6
358 (+6,-4)	36.4
346 (+2,-3)	100.0
329 (+1)	7.4
195 (+4,-4)	35.8
181 (+7,-7)	41.6
167 (+6,-7)	44.3
153 (+4,-6)	36.0
141 (+4,-10)	40.8

[Values in parenthesis denote lines on each side of quoted line]

4.4.5 Coupling Attempt of C,C' - dilithio- and C,C' - diiodo-m-carborane promoted by a copper (II) catalyst:

0.043 mol of dilithio-m-carborane, filtered and washed, was taken up in 50 ml of pre-cooled ethylene glycol dimethyl ether containing 0.002 mol of anhydrous cupric chloride. To the solution at 0°C was added 0.033 mol of diiodo-m-carborane over a 60 minute period. The light yellow colouration of the iodoinated compound changed to red-brown during addition and, after addition, assumed a beige colouration.

The reaction temperature was raised, after a 3 hour residence at 0°C, to ambient, at which stage the reaction appeared to develop a slight exotherm. After several hours the reaction mixture was warmed to 64°C for 2 hours and termination effected by hydrolysis at 0°C. After separation, washing drying and evaporation of the organic phase, 18.120 g of dark oil was collected as the crude product. Overnight standing of the oil resulted in a precipitation of solid matter.

Separation efforts consisted of filtration of the solid matter from the crude product, giving rise to 8.906 g of beige oily solid, and the remaining product in the form of a dark oil.

Both fractions were subjected to sublimation at 65°C, giving 6.736 g of sublimed material from the solid portion and 1.907 g from the oil component. Chromatographic identification indicated the sublimed materials in both instances to comprise the starting materials solely ($R_f \sim 0.8$). Additionally, the unsublimed portions of these products appeared from TLC to be of identical composition, starting material at R_f 0.8, a product fraction at $R_f \sim 0.4$ and a series of low R_f valued components, to $R_f \sim 0.2$. The two portions were therefore recombined and exhaustively extracted with n-hexane and benzene, and 0.417 g of beige solid as extracted material, leaving 0.033 g of insoluble matter. Crystallisation attempts of the hexane-soluble portion from that solvent produced only two small fractions (0.046 g total) with composition appearing similar to the crude product from TLC observations.

4.4.6 Coupling Attempt of C,C'-Dilithio-m-carborane Assisted by a Copper(I)/Copper(II) System:

Lithiated m-carborane, 0.154 mol, filtered and washed, was taken up in 350 ml of diethylene glycol dimethyl ether (vessel(1) figure 9) and the temperature lowered to -70°C. To the solution was added 0.144 mol of pretreated cuprous iodine (*via* flask (6) and adaptors(5)) over a 45-minute period with stirring. After 3 hours at this temperature, the reaction setup was raised to ambient. This temperature rise resulted in a colour change from a milky white solution to a dark (green-grey) oil. A two-phase solution resulted, and difficulties were encountered with stirring. After 15 minutes, the temperature was again lowered to -70°C, and 0.144 mol of pretreated cupric chloride was added over a 30 minute period in the same manner as the copper(I) salt. The reaction solution, upon reaching room temperature overnight, still appeared heterogeneous, but the lower oily phase, having assumed a dark green colouration, had become considerably less viscous. After raising the temperature to approximately 54°C for 1 hour, the reaction was terminated by hydrolysis at ice bath temperature. The crude product obtained in this fashion appeared as a tacky brown-green material, total 36.11 g.

First impressions of the product composition, from TLC observations, indicated the majority of the components comprised the high R_f valued bands, *viz* $R_f \sim 0.8$, with minor proportions occurring at $R_f \sim 0.7$, $R_f \sim 0.4$ and a tail at $R_f \sim 0$ to 0.2. The unexpected ultra-violet development of some of these components suggested a halogenated product composition. The first separation attempt consisted of subjecting 80% by mass of the crude product to column chromatography on a 27 cm x 4.5 cm diameter column of alumina.

Twenty-three fractions were obtained in this fashion. The first ten, in 100 ml-portions, stemmed from the use of a n-hexane eluent, which extracted the bulk of the starting material band at $R_f \sim 0.8$ (14.229 g total). The following four fractions (a 200-ml and 3 100-ml portions) employed hexane: benzene (9:1) as eluent and appeared also to consist of the starting material in essence (0.329 g total). Hereafter, the fractions collected, with benzene concentration gradually increased to 100%, resulted in a yellow oil product containing a concentrated proportion of the lower R_f bands, but no significant separation was observed. Subjecting the bulk of the last mentioned fractions, in all 0.585 g (but excluding the benzene-eluted portion, 0.192 g), to crystallisation from n-hexane yielded four crystalline fractions (0.046 g total) in the TLC observed range of $R_f \sim 0.4$. The melting points of these white crystals were typically observed at 101.[illegible]° - 104.0°C. Mass-spectroscopic analysis detected a major peak distribution at the mass number for mono-iodo-m-carborane, i.e.,~272 (Lit[22] mp 105° - 105.5°C). The remaining yellow oil yielded no further crystalline products.

From the remaining 20% of the crude product was obtained 4.174 gof white solid hexane-solubles and 0.176 g of benzene-solubles in the form of a yellow oil. Sublimation at 65°C of the hexane-soluble material gave 3.487 g of sublimed material consisting primarily of the $R_f \sim 0.8$ band in addition to minor quantities in bands at $R_f \sim 0.4$ and ~ 0.2. The unsublimed product portion collected, 0.280 g of cream coloured solid appearing to be concentrated in the band at $R_f \sim 0.7$, was taken up in hot hexane in an attempt to crystallise. The last of five, crystal fractions, 0.093 g of silvery white crystalline matter, $R_f \sim 0.7$, gave a melting point of 264.0° - 267.5°C. In equal proportions with the known bi-*m*-carborane, a mixed melting point of 262.7° - 268°C was obtained, indicating the products to be of the same composition.

4.4.7 CouplingAttempt of C,C'-Dilithio-*m*-carborane Assisted by a Copper(II) System:

The liquor containing the reaction products of 0.028 mol of *m*-carborane and 0.056 mol of butyllithium in 250 ml of diethyl ether was cooled to -70°C (vessel(1) figure 9) and treated over 15 minutes with 0.056 mol of anhydrous deaerated cupric chloride (flask(6), adaptors(5)). During this addition stage the reaction liquor assumed a green colouration. The mixture was permitted to achieve room temperature at which it was run overnight. 250 ml of pretreated tetrahydrofuran was added to the flask (funnel(4)), the ether distilled off, (apparatus (12), and the reaction run for 4 hours at 60°C and then at room temperature overnight followed by hydrolysis at 0°C, at which stage the solution became clear, with green solid suspension. Diethyl ether (200 ml) was employed to achieve phase separation of the hydrolised solution. While running the organic phase to dryness (after drying over $MgSO_4$) a white crystaline solid precipitation from solution, collected separately. The remaining organic phase yielded 0.265 g yellow solid (mp 245^{o} - $255^{o}C$).

TLC analysis of the precipitated fraction, recrystallised from n-hexane, indicated the product to be comprised primarily of two products, namely the band at $R_f \sim 0.8$ (starting material) and that at $R_f \sim 0.7$, in apparently higher concentration than the former. The product contained in the $R_f \sim 0.7$ band was separated from the mixture by hexane crystallisation, making its appearance in the first few fractions as white crystals yield 1.506 g mp (typical) 260^{o} - $266.3^{o}C$, mixed with *m*-carborane gave a depressed mixed melting point 192.6^{o} - $212.2^{o}C$ and mixed with known dimer gave no depression (267^{o} - $270^{o}C$). Recrystalisation from hexane gave fine white crystals of typical mp 270.7^{o} - $272.2^{o}C$

Recrystallisation of another product portion from benzene similarly yielded this product in its pure form, mp 271.0° - 272.2°C. Total yield of the bi-m-carborane product in its pure state was 1.311 g, or 30% conversion from m-carborane Mass spectra of the compound (Refer § 3.7) gave a predominant peak distribution around m/e 285 and a minor distribution around m/e 141. Infrared spectroscopy (refer § 3.7) resulted in absorption peaks at 3020, 1130, 1080, 1040, 750, and 720 cm^{-1}.

Other product portions containing the starting material, low R_f compounds and the dark oily benzene- and hexane-insolubles were not investigated further.

4.4.8 Less Successful Variations in the Coupling Attempt Involving C,C'-Dilithio-m-carborane Assisted by Copper(II) Chloride :

4.4.8.1 Solid lithiated m-carborane in ether/benzene solvent medium :

Lithiated m-carborane (40% conversion obtained as described in 4.3.2 alternative [C]), 0.005 mol, was taken up in 125 ml of diethyl ether and 8 ml of benzene and to it was added at -20°C over a 30 minute period an excess of anhydrous cupric chloride (0.020 mol). The solution was gradually raised in temperature to ambient, following this, refluxed for 10 minutes over a steam bath. Hydrolysis, separation, drying over $CaC\ell_2$ and evaporation yielded 0.651 g of a tacky brown material. Sublimation at 70°C recovered 0.064 g starting material, and the remaining crude product was digested in hot hexane and the residual in hot benzene. (Benzene solubles, 0.060 g of grey solid, gave rise to mp 350°C). The hexane-soluble fraction was subjected to crystallisation from that solvent yielding brown solid matter (0.310 g) of typical mp's. 165.0°C to 207.6°C. TLC observations indicated the principal reaction product components to be the starting material ($R_f \sim 0.8$), the dimer ($R_f \sim 0.7$) and minor amounts of supposedly higher oligomers often appearing as tails on our plates attached to the dimeric compound. Repeated recrystallisations generated 0.096 g [ΛI], mp 270.2° - 272.0°C.

4.4.8.2 Oxygen Introduction :

Lithiated m-carborane (§4.3.2-[C]) 0.043 mol was taken up in 150 mol of dimethoxy ethane and, at a reaction temperature of -70°C, approximately half of the 0.040 mol of cupric chloride was added over 10 minutes, maintained at -70°C for 10 minutes, raised in temperature to ambient for 15 minutes (approx) and cooled to -70°C. The remaining cupric chloride was then added (20 minutes) the reaction kept at -70°C for 2 hours. Oxygen was then passed through the solution for 20 minutes. After an overnight rise in temperature to ambient the solution was heated for 45 minutes at 53°C, cooled to 0°C and hydrolysed in the standard fashion. After sublimation (50°C removing 0.522 g starting material) the residue (6.272 g, organge/yellow compound) was subdivided into hexane-and benzene-soluble portions. The hexane-solubles crystalised from the mother liquor 1.455 g of white solid material (mp 198.7° - 239.3°C example). TLC studies indicated these components to comprise base spots on the slides appearing white under both UV and iodine developments with tails extending to $R_f \sim 0.6$. Evaporation of the above mother liquor resulted in an orange oil which precipitated 0.256 g white solid. TLC analysis indicated the dimer ($R_f \sim 0.7$) to be present as well as starting material and some lower bands. Two fractions crystallised from hexane, 0.045 g, yielded [XI], mp 270.5° - 272.5°C. The benzene soluble portion, 3.370 g, crystallised from benzene, giving 0.081 g of cream-white crystals, mp 138.0° - 202.3°C, 0.063 g of white fine crystals, mp $>$ 350°C and 1.494 g of white fine crystals (mp not determined). [The latter failed to return to benzene but was found to be soluble in ether, ethanol, acetone, chloroform, acetonitrile and dimethoxyethane]. The first fraction crystallising from benzene (base spot on TLC; UV and I_2 devel.) precipitated from a controlled ethanol-water mixture white fine crystals which were indicated by mass spectroscopy, to be mono-hydroxy-m-carborane (ref. § 3.7, fig. 8).

5. SUMMARY: CONCLUSIONS AND RECOMMENDATIONS

It is the goal of the work undertaken in this dissertation to establish a feasible approach to direct carbon-carbon coupled dimeric carborane species, to serve as a basis for future extension to polymeric synthesis. The meta-carborane isomer (1,7-dicarba-closo-dodecaborane (12)) was selected for this purpose, in the light of its more attractive coupling profile compared with the ortho-isomer, and its availability, compared with the para - compound. The experimental approaches encompassed coupling procedures of the Ullmann reaction, ionic coupling attempts (including catalytic promotion) and the coupling of lithiated m-carborane.

An overview of our efforts is as follows: The use of diiodo-m-carborane with copper bronze in the Ullmann coupling attempt is unsuitable from the aspect of the steric effects associated with this molecule, and also in view of insufficient delocalization of electronegativity of the molecule. The direct ionic coupling approach to dimerisation employing the dilithio- and diiodo-derivatives of m-carborane underwent no detectable reaction in the desired direction. Evidence of substitutent interchange was noted in these processes, and, although traces of oligomeric by-products were observed, separation proved highly impractical owing to a multitude of degraded or oxidised reaction products. Maintaining the concept of ionic coupling of the species, promotion of the process was attempted by the introduction of catalytic quantities of palladium chloride in the next experimental phase with minimal success. The reaction products appeared essentially similar to the preceeding experiments, the minor differences in composition being attributed to the methods of sampling and levels of purity, rather than to the process itself. The final attempt at ionic dimerisation, employing a cupric chloride catalytic system, yielded very much the same results as above, and led us to conclude the iodinated carborane species to be the thwarting factor in these efforts. It appears from some of the strictly carborane oligomeric materials obtained that the iodinated species is unsuitable as an ionic partner to the lithiated derivative, the latter being more practical to auto-coupling. We surmise this is the result of the covalent nature of the carbon-iodine bond in the iodocarborane.

Dispensing with iodinated derivatives of carborane, our attempts were directed at the promotion of the auto-coupling capabilities of dilithio-m-carborane by assistance of copper salts. The use of the dual system of cuprous iodide and cupric chloride gave rise to the formation of bi-m-carborane, but in only minor quantities. The process in these instances appeared severely hampered by the formation iodinated by-products, from copper (I) iodide, whilst no such interference was observed from the chlorine atoms of copper (II) chloride. By employing cupric chloride alone as an assist vehilce in our coupling attempts we were finally able satisfactorily to synthesise the dimeric *meta*-carborane species.

Optimum yields of bi-*m*-carborane were obtained from the reaction of the dilithiated monomer with copper (II) chloride in tetrahydrofuran under rigourously controlled anhydrous and anaerobic conditions. Dimerisation was effected by heating to ~ 60°C and the reaction terminated by mild acid hydrolysis. The product [XI] was readily isolated and purified by recrystallisation. In this manner, 30% conversion of *m*-carborane (to the pure and isolated dimeric compound) was achieved. Product identification was accomplished by mass spectroscopy, infra-red spectroscopy and chromatographical observations.

It is suggested that the described system of bi-*m*-carborane synthesis be employed as a basis for the development of directly interlinked polymeric carborane structures. These investigations should employ over-lithiated carborane species to promote conversion, possibly employing a 3:1 or

4:1 ratio of butyllithium to carbon. The reaction conditions, in terms of alternative coupling media and the use of higher reaction temperatures, should additionally be investigated in the optimisation of coupling and aiding of polymeric carborane synthesis. As our attempts at achieving dimerisation were restricted to copper assistance we would furthermore suggest alternative assist systems be employed in these investigations, eg., nickel or mercuric salts. Finally, we recommend co-use of crown ethers as alkali cation binders for enhanced availability and accessibility of the carborane anions in these extended coupling reactions.

APPENDIX

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