FOUR DECADES OF ORGANIC CHEMISTRY OF closo-BORANES: A SYNTHETIC TOOLBOX FOR CONSTRUCTING LIQUID CRYSTAL MATERIALS. A REVIEW

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Dedicated to Dr Stanislav Heřmánek on the occasion of his 70th birthday in recognition of his outstanding contributions to the areas of borane chemistry and NMR spectroscopy.

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Introduction and transformations of organic functional groups to ten- and twelve-vertex closo-boranes and heteroboranes is reviewed in the context of preparation of liquid crystalline compounds. The review, containing 198 references, is designed as a synthetic manual for materials chemists and focuses on methods for engineering molecules with elongated shapes and variable dipole moments. Several underdeveloped aspects of closo-borane chemistry are identified.

Key words: Boranes; Carboranes; Heteroboranes; Clusters; Liquid crystals.

1. INTRODUCTION

The synthesis of the first organic derivatives of closo-dodecaborate (1, Fig. 1) and closo-decaborate 7 in 1962 (ref. 1) followed by a number of organic derivatives of ortho-carborane 4 (refs 2,3) and meta-carborane 5 (ref. 4), signaled the beginning of an exciting period for closo-borane chemistry and applications of inorganic-organic hybrid materials 5. High chemical, thermal and electrochemical stability of the ten- and, especially, twelve-vertex closo-
boranes\textsuperscript{6} (Fig. 1) have been utilized in preparation of thermostable polymers\textsuperscript{7}. The low toxicity\textsuperscript{8} of closo-borates \textsuperscript{1} and \textsuperscript{7} makes them suitable for biomedical applications such as boron neutron capture therapy\textsuperscript{9,10}. More recently, boron clusters have been used as non-nucleophilic anions\textsuperscript{11} and for molecular materials such as molecular-scale construction sets\textsuperscript{12-14}. Exploration of boron clusters as structural elements for liquid crystals is the most recent chapter in the chemistry and application of closo-boranes\textsuperscript{15}. So far only several of the ten clusters, decaborate \textsuperscript{7} (refs\textsuperscript{16,17}), monocarbaborate \textsuperscript{2} (ref.\textsuperscript{18}), and para-carboranes \textsuperscript{6} and \textsuperscript{10} (refs\textsuperscript{17,19-23}), have been used in the synthesis of liquid crystals. The results obtained to date\textsuperscript{15} demonstrate the structural versatility of these compounds and their enormous potential in the study of the phenomenon and applications of liquid crystals.

The rich chemistry of the clusters in Fig. 1 and the understanding of their properties has been driven by scientific curiosity and materials demands and described in several reviews\textsuperscript{6,24-31}. Here we will concentrate on the transformations of closo-boranes that lead to disubstitution in the antipodal position giving electrically neutral molecules with the most extended molecular shapes which are prerequisite for liquid crystalline behavior\textsuperscript{15}.

**Fig. 1**
Skeletal representations of the borates (1, 7), monocarbaborates (2, 8), azaboranes (3, 9), ortho-carborane (4), meta-carborane (5), and para-carboranes (6, 10) shown with chemical formulas. In the structures each vertex corresponds to a B–H fragment and the CH and NH groups are marked by open and filled circles, respectively.
2. PREPARATION OF THE PARENT CLUSTERS

Commercially available decaborane(14) (11) is the common precursor to all ten clusters 1-10 as shown in Scheme 1. Generally the twelve-vertex closo-clusters are more convenient to prepare than the ten-vertex analogs. For the former, insertion reactions are typically used, while the synthesis of the ten-vertex clusters involves selective degradation processes of the eleven- and twelve-vertex species.

The transformation of \([B_{10}H_{14}]\) (11) to the anions 1 (ref. 32) and 7 (ref. 33) were the first syntheses of the closo-skeleton which involved borane insertion34 or amine-induced dehydrogenation35 reactions, respectively.

The twelve-vertex ortho-carborane 4 (ref. 2) has been obtained by acetylene insertion to decaborane 11 (refs 36, 37). Reaction of substituted acetylenes provides a convenient route to mono- and disubstituted derivatives of 4 (refs 2, 38, 39).
Thermolysis of ortho-carborane 4 at 465–500 °C (ref.4) or in a flow system at 600 °C (ref.40) produces the meta isomer 5 in high yield4, while higher temperatures give an equilibrium mixture of para-carborane 6 and its meta isomer. The para isomer 6 (ref.41) can be separated chromatographically42, taking advantage of the difference in the polarity43 (2.85 D for 5) or by selective conversion of the meta isomer to the \([C_2B_9H_{12}]^+\) nido anion (12, Scheme 2)44. This latter method is particularly convenient for large-scale preparations of 6.

Some C-substituted meta-carboranes, but not para-carboranes, have been obtained by thermal rearrangement of the corresponding C-substituted ortho-carboranes. This method is limited to methyl4, ethyl45, and phenyl46 derivatives while other alkyls45 and functional groups4 show limited thermal stability.

2-Substituted meta-carboranes 13 have been efficiently prepared either by RBCl2 \((R = \text{Ph} \text{ (ref.47), } R = \text{C}_6\text{H}_{4}-4-\text{Me (ref.47), } R = \text{C}_6\text{H}_{4}-4-\text{F (ref.47), } R = \text{vinyl (refs48,49), and } R = \text{F (ref.50)})\) insertion reaction into the nido anion 12 or skeletal rearrangement of 3-substituted ortho-carboranes 14. Flash vacuum thermal rearrangement of 3-CN, 3-NH2, 3-OH, and 3-F (ref.50) derivatives of ortho-carboranes 14 gives good yields of equimolar mixtures of the 2- and 4-substituted meta-carboranes, which can be separated using chromatographic methods50,51.

Ten-vertex para-carborane52 10 has been obtained in a similar way to its twelve-vertex analog 6 by thermal rearrangement of the corresponding ortho-carborane 15a via the meta isomer at the relatively low temperatures of 330–350 °C (Scheme 3)52. The ortho-carborane 15a is prepared by thermal53 or base-induced dehydrogenation54,55 of nido-carborane 16a obtained either through sequential deboronation54,56 of twelve-vertex ortho-carborane 4 or by acetylene insertion57 to B3H13(SMe2). The overall yield of para-carborane 10 is 30–50% based on the starting ortho-carborane 4.

Preparation of C-substituted para-carboranes generally follows the preparation of the parent carborane 10 and it takes advantage of the relatively

---

**Scheme 2**

\[ \text{5 KOH} \xrightarrow{1. BuLi} \text{12} \xleftarrow{2. RBCl_2} \text{13} \xrightarrow{550^\circ \text{C}} \text{14} \]

---

Monocarbaborate anions 2 and 8 were prepared relatively early\(^{61,62}\) and several reviews on their chemistry and properties have recently appeared\(^{11,28,31}\). The carbon atom is introduced as a nitrile ligand to form arachno adduct 17 (Scheme 1), which, upon hydrolysis and partial degradation with HCl, yields a mixture of nido amines [7-NH\(_3\)-CB\(_{10}\)H\(_{12}\)] (18) and [6-NH\(_3\)-CB\(_9\)H\(_{11}\)] (19) in proportions dependent upon the reaction conditions\(^{63-65}\). N-Methylation followed by dehydrogenation-deamination of the latter using piperidine yields 8 (ref.\(^{56}\)), while 18 requires borane insertion and sodium metal cleavage of the [1-NMe\(_3\)-CB\(_{11}\)H\(_{11}\)] to furnish 2 (ref.\(^{63}\)).

C-Amino substituted monocarboranes 20 and 21 have been obtained in good yields via borane insertion to [7-NH\(_3\)-CB\(_{10}\)H\(_{12}\)] (18) (ref.\(^{67}\)) and borane-induced dehydrogenation of [6-NH\(_3\)-CB\(_{9}\)H\(_{11}\)] (19) (ref.\(^{68}\)), respectively. Borane insertion reactions to [7-SMe\(_2\)-CB\(_{10}\)H\(_{12}\)] (ref.\(^{67}\)) or [7-NMe\(_2\)-CB\(_{10}\)H\(_{12}\)] (ref.\(^{65}\)) result in demethylation and products [1-SMe-CB\(_{11}\)H\(_{11}\)] and [1-NMe\(_2\)-CB\(_{11}\)H\(_{11}\)], respectively, have been obtained. The latter is also obtained in 61% yield in the cage expansion reaction of [1-NMe\(_2\)-CB\(_9\)H\(_9\)] with borane\(^{68}\).
The newest addition to the pool of closo-heteraboranes are the aza-
boranes\(^69\). Unlike the synthesis of 9 (ref.\(^70\)), the preparation of the parent
\([\text{NB}_{11}\text{H}_{12}]\) (3) is rather inefficient and involves the dangerous hydrazoic
acid\(^71\). N-Substituted derivatives are easily prepared using the correspon-
ding amines and \([\text{B}_{9}\text{H}_{13}(\text{SM}_{2})]\) via the nido derivative 22 (Scheme 1)\(^69\). Sub-
sequent thermal dehydrogenation of 22 yields ten-vertex derivatives 9R
(ref.\(^72\)) whereas borane insertion to 22 leads to the corresponding 3R deriv-
atives\(^73,74\).

3. FUNCTIONALIZATION OF THE TEN- AND TWELVE-VERTEX CLUSTERS

Over the last 35 years the chemistry of all ten boron clusters 1-10 has been
well advanced and methods for substitution at the boron, carbon, and ni-
trogen sites have been developed. Among the clusters, the twelve-vertex
carboranes 4-6 and borates 1 and 7 are the most studied, largely due to their
availability. Least investigated are monocarbaborate 8 and the re-
cently prepared azaboranes 3 and 9, which are less readily available due to
more complicated syntheses.

The hydrogen atoms on the endoskeletal carbon and nitrogen atoms in
2-6 and 8-10 exhibit protic character (e.g., \(pK_{a}=26.8\) for 6 and 27.3 for
10\(^75\)). They can easily be removed using alkyllithiums\(^25\), LDA (ref.\(^13\)), and
t-BuOK (refs\(^13,76\)) giving rise to highly nucleophilic heteroanions (C-anions
or N-anions). The skeletal B–H groups undergo electrophilic substitution re-
actions with a variety of electrophiles with the preference for the antipodal
position to the heteroatom.

In principle, substitution and chemical transformations of the boron, car-
bon, and nitrogen centers are transferable between the clusters and be-
tween the ten- and twelve-vertex series, although differences in reactivity
and regiochemistry are occasionally observed. For instance, carbon chemis-
try developed for ortho- and meta-carboranes and described in previous re-
views\(^25,27\) is applicable to the less available para-carboranes 6 and 10 and, to
a large extent, to monocarbaborates 2 and 8. On the other hand, stable
dinitrogen derivatives are unique to decaborate 7 although several clusters
undergo synthetically useful diazotization-substitution reactions (vide infra).

From the liquid crystal point of view, substituents such as n-alkyl, n-alkoxy, n-alkythio, cycloalkyl and aryl and functional groups such as
esters, nitriles, Schiff bases and azo groups are particularly useful structural
elements\(^77-79\). Judicious choice of these groups allows for modulation and
tuning of thermal, optical and dielectric properties of the materials. Here
we will concentrate on synthetic methods that allow for introduction of
these substituents onto the boron cluster. The chemistry of azaboranes will be omitted in the following discussion. Although azaboranes 3 and 9 can be N-alkylated and B-halogenated they exhibit rather significant sensitivity to solvents and nucleophiles and their usefulness for materials purposes is questionable.

3.1. Carbon Substitution

Carbon–carbon bonds. Carborane and monocarbaborate-derived anions are highly nucleophilic and react with a wide range of C-electrophiles providing a convenient route to C–C bonds. The C-lithium reagents are particularly useful in the alkylation with primary iodides and bromides and carboxylation reactions described for carboranes including para-carboranes 6 (refs 20, 82, 83) and also for monocarbaborates 2 (refs 57, 86) and 8 (ref. 61). The preparation of 12-pentyl-para-carborane-1-carboxylic acid (23, Scheme 4) is an example of both processes. It also demonstrates our recently developed strategy for efficient differentiation of the two carbon atoms in 6 using a Ph3Si substituent, which induces crystallinity and UV activity facilitating isolation, purification and storage of the products and intermediates. Other methods for hetero-disubstitution in 6 (refs 87, 88), 10 (ref. 12), and 4 (refs 89, 90) are less general.

Carboranylcopper reagents 24 provide excellent means for the preparation of C-aryl 25, C-vinyl 26 (ref. 91), and C-acetylene 27 (refs 23, 82, 91) derivatives (Scheme 5). Unlike the carboranylolithiums, the carboranylcopper reagents do not equilibrate with the C–H acid form and high degrees up to 80% of monoaarylation of 6 have been obtained. The original Wade procedure for arylation of the twelve-vertex carboranes has been extended to arylation and ethynylation of the ten-vertex para-carborane 10. Attempts to use the procedure for the introduction of perfluoroalkyl de-
derivatives proved unsuccessful, and only carboranyl halides 28 (bromides and iodides) were obtained in the metal–halogen exchange process (Scheme 5). A similar metal–halogen exchange reaction is also observed with some acetylene iodides and bromides.

It appears that carboranycoper species are the only effective reagents in arylation reactions. Ten-vertex carboranyl zinc is the only exception found so far, and it reacts with 4'-cyano-4-biphenyl triflate under the Negishi reaction conditions, giving a modest yield of the coupling product 29 (ref. 95). The analogous Pd-catalyzed coupling reactions of twelve-vertex para-carboranyllithium 97,98 or stannane 13 with iodobenzene or with aryl triflates were unsuccessful and no coupling product was observed.

Among other carbon electrophiles that react with carboranyl anions are PhOCN, preferred for preparation of the ten-vertex para-carborane nitriles 97, and tosyl cyanide, the reagent of choice for synthesis of twelve-vertex carboranenitriles 98.

The reaction of orthoformates with ten-97 or twelve-vertex 88,99 carboranyllithium yields carboranyl acetics which are easily converted to the corresponding aldehydes. For instance, para-carborane-1,12-dicarb-
aldehyde was obtained in 23% overall yield based on para-carborane 6 (ref.99). The reaction of para-carborane 6 under controlled conditions gives a non-statistical yield of acetal 30, which is converted to 12-hydroxy-para-carborane-1-carbaldehyde (31) via boronic acid 32 (Scheme 6)88.

A special case of the C–C bond formation is the dimerization reaction of para-carborane. Oxidative coupling of either ten-12,84 or twelve-vertex12,100,101 carboranyllithium with anhydrous CuCl2 gives a high yield of the desired dimeric product 33. If more than one equivalent of BuLi is used then higher oligomers are formed12,101.

Carbon–nitrogen bonds. There are relatively few examples of C–N bond formation. Direct amination of dilithio-para-carborane with MeONHLi has been reported to give a mixture of the 1-amino- and 1,12-diamino-para-carboranes87. Attempts to extend this procedure to [12-(n-C7H15)-1-Li-CB11H10] resulted in only traces of the desired 1-amino product 94.

An alternative approach to the desired C-amino carboranes utilizes the acid-catalyzed cleavage of triazines that can be obtained from carboranyl-lithium and phenylazide in about 80% yield102.

C-Nitrosylation of para-carboranyl-lithium with NOCl was reported to proceed in about 30% yield103. C-Nitrosylation of monosubstituted ortho- and meta-carboranyl-lithium occurs in good yield and meta-carboranyl-lithium can be dinitrosylated in 30% yield104,105. Attempted C-nitrosylation of [12-(n-C7H15)-1-Li-CB11H10] was unsuccessful94.
Reactions of ortho- or meta-carboranyllithium with a benzenediazonium salt yield the corresponding azo derivatives such as 34, which exhibit remarkably high thermal and chemical stability\textsuperscript{106,107}.

Catalytic reduction of azocarboranes\textsuperscript{107} is a recommended method for the preparation of C-amino derivatives and is preferable to the reduction of C-nitroso\textsuperscript{104} or C-nitro\textsuperscript{85} compounds.

Carbon–sulfur bonds. Formation of the C–S bond can be effected by treatment of the C-lithium or C-sodium derivatives of ortho-carborane 4 (\textsuperscript{89,108–111})\textsuperscript{,} meta-carborane 5 (\textsuperscript{108,109,111})\textsuperscript{,} para-carborane 6 (\textsuperscript{82,103,109,111,112})\textsuperscript{,} and monocarbaborate 2 (\textsuperscript{67}) with elemental sulfur\textsuperscript{67,89,103,108–112}, sulfur dioxide\textsuperscript{103,108}, dialkyl disulfide\textsuperscript{110}, or alkylsulfenyl halides\textsuperscript{82} as shown for 35.

The C–S bond has rather limited stability. Lithium salts of the carboranethiols in benzene and aqueous carboranesulfinic acids undergo thermal desulfurization above 50 °C (\textsuperscript{108}). Alkylthio derivatives such as 35 undergo partial decomposition on silica\textsuperscript{82} and are susceptible to attack and cleavage by alkyllithiums\textsuperscript{110} and fluoride anion\textsuperscript{82}. 1-Alkylthio-ortho-carboranes, however, have been reacted with BuLi and converted into the corresponding C-anions in high yields\textsuperscript{113}.

Carbon–oxygen bonds. Direct C-oxygenation has been accomplished by reacting carboranyllithium with oxygen\textsuperscript{114} or peroxides\textsuperscript{115} among which trimethylsilyl peroxide was found to work best, giving yields of the C-hydroxy-para-carborane up to 30% (\textsuperscript{88,116}). An even more efficient method for introduction of the hydroxy group through the oxidation of the corresponding C-boronic acid was reported recently (Scheme 6)\textsuperscript{88}. The sequence of reactions starting from 30 gives 12-hydroxy-para-carborane-1-carbaldehyde (31), a carborane analog of 4-hydroxybenzaldehyde, in 88% of overall yield.
Carbon–halogen bonds. There are relatively few examples of the formation of C–halogen bonds. The C-halogenation reaction is highly efficient\(^{85,103,117}\) and occasionally observed as an undesired processes (vide supra). The C–I compounds have limited synthetic utility (vide infra)\(^{118}\) while the C–F and C–Cl compounds may be used to increase molecular dipole moments\(^{119}\) and to introduce axial chirality in 2,9-disubstituted meta-carboranes. All C-halogen derivatives are susceptible to base-induced dehalogenation.

Carbon–mercury bonds. Reaction of ten- or twelve-vertex para-carboranyl anion with mercury(II) halide leads to the formation of a stable dicarboranyl mercury, e.g. 36, with an extended molecular shape\(^{13,103,120}\). The anion has been generated using alkylithiums\(^{120}\) or LDA (ref.\(^{13}\)) and reacted with mercury halide or formed in situ with potassium tert-butoxide in DMF in the presence of HgBr\(_2\) (ref.\(^{13}\)).

\[
\begin{align*}
\text{Ph} & \quad \Delta \quad \text{Ph} \quad \text{BuLi or} \quad \text{LDA or} \quad t\text{-BuOK} \\
\text{1} & \quad \rightarrow \quad \Delta \quad \text{Hg} \quad \text{Ph} \\
\text{2} & \quad \text{HgBr}_2 \quad \text{80%} \\
\text{36} & \quad \text{Hg} \\
\end{align*}
\]

3.2. Boron Substitution

The regiochemistry of electrophilic substitution in boron clusters is frequently complicated by the presence of two or more types of boron atoms in the cage. Although one position in the cage typically has higher electron density and is thermodynamically preferred (B(2) in 6 and 10, B(9) in 4 and 5, B(1) and B(10) in 7, B(10) in 8 and 9, B(12) in 2 and 3), the substitution occasionally occurs at kinetic sites (vide infra). The regioselectivity of substitution depends on the cluster, type of electrophile, and, occasionally, reaction conditions.

There are two general types of electrophiles which react with a negatively charged cluster to yield either charged or electrically neutral products as shown for a monocarbaborate in Fig. 2.

\[
\begin{align*}
\text{E} & \quad \text{E}^+ \\
\text{E}^- & \quad \text{E}^+ \quad \text{E}^- \\
\end{align*}
\]

Fig. 2
Substitution with electrophiles E\(^+\) or E\(^-\) shown using the monocarbaborate as example
Among the electrophilic reactions, iodination, diazotization, metallation, and sulfurization reactions provide particularly valuable and versatile intermediates in the context of synthesis of liquid crystals. Other reactions are much less selective or preferentially yield the undesired regioisomers.

Boron–iodine bonds. Iodination of the clusters typically proceeds in high yield and with high regioselectivity for the thermodynamic position. The reaction rate and the conditions depend on the type of the cluster; charged clusters undergo iodination under mild conditions while neutral boranes and, in particular para-carborane 6, require Lewis acids as catalysts. Monoiodination of 1-methyl- and 1-phenyl-ortho-carborane yields a mixture of 12- and 9-iodo derivatives, 37 and 38, respectively, from which the desired 12-iodo isomer 37 can be separated chromatographically. Diiodination of para-carborane 6 proceeds in high yield but lacks selectivity and the desired 2,9-isomer 39 has been isolated in only 11% yield (Scheme 7).

Iodination of twelve-vertex monocarbaborate anion 2 proceeds in a high yield and is highly selective for the 12-position. Similarly, iodination of quinuclidine derivative 40 with ICI predominantly yields the 12-iodo derivative 41 in 40 or 73% yield based on recovered starting material. Iodination of the 1-NMe₃ analog with I₂ and AlCl₃ as the catalyst was reported to give 81% yield of the corresponding 12-iodo product.
Reaction of I₂ with [1-NMe₂-C₅B₁₁H₁₁] under basic conditions led to the N-demethylation product 129.

Iodination as well as other halogenation reactions of ten-vertex analog 8 exhibits high regioselectivity for the 6 position and the desired 10-ido-1-carba-closo-decaborate (42) is formed in less than 2% yield¹³⁰. It has been proposed that the latter may be obtained by thermal rearrangement of the kinetic 6-isomer 43 isolated in 51% yield¹³⁰.

Boron–nitrogen bonds. The formation of stable dinitrogen inner salts is specific to the [B₁₀H₁₀]²⁻ anion (7) and no other cluster has been reported to form such derivatives. Thus diazotization of 7 with nitrous acid followed by reductive workup yields about 15–25% of the 1,10-bis(dinitrogen)-closo-decaborane (44) as the only product¹³¹. The uniquely high isomeric purity of the isolated 44 and other analogous compounds¹³²,¹³³ is not necessarily related to the high regioselectivity of the substitution. It is more likely that other isomers are formed but only the 1,10-isomer is stable enough to be isolated. Our ab initio calculations support this hypothesis showing that the apical N₂ group is twice as stable to heterolytic cleavage than that in the equatorial position⁹⁶.

Reaction of the closo-decaborate anion (7) with one equivalent of arenediazonium salts to form azo compounds 45 is another example of a transformation unique to this cage and highly regiospecific for the apical position¹³⁴,¹³⁵. The observation that certain aryl groups eliminate under weakly basic conditions yielding the dinitrogen derivatives allowed for selective preparation of 1-dinitrogen-closo-decaborate (46) and differentiation of the apical position¹³⁶,¹³⁷.
This method also permits the introduction of the dinitrogen to the substituted decaborate monoanions providing an invaluable tool for hetero-disubstitution of 7 (vide infra)\textsuperscript{136}. For instance, dinitrogen derivative 47 was obtained from the anion 48 in \textasciitilde50\% yield using the Hawthorne method\textsuperscript{136}, while diazotization–reduction sequence of the Knoth method\textsuperscript{131,132} is only half as efficient\textsuperscript{16}.

Direct electrophilic amination reactions of charged boranes yield the kinetic meta isomers as the major products and only traces of the desired para isomers are formed. Reaction of closo-dodecaborate anion 1 with hydroxylamine-O-sulfonic acid results in the formation of small quantities (<10\%) of the desired 1,12-diamine\textsuperscript{138,139}, while the same reaction for the ten-vertex analog 7 yields equatorial diamines only\textsuperscript{138}. Similar results are obtained for hydroxylatation reactions with amides and sulfones\textsuperscript{140,141}.

Amination of monocarbaborate 2 with hydroxylamine-O-sulfonic acid gives only traces of the desired 12-amino isomer and the meta isomer is the sole product in addition to the recovered starting 2 (ref.\textsuperscript{142}).

Boron–metal bonds. Metallation of twelve-vertex boron closo-clusters with mercury or thallium trifluoroacetates occurs at the thermodynamic position with high selectivity\textsuperscript{143,144}. Parent and substituted carboranes 4 and 5 yield 9-metallo derivatives (e.g. 49) and para-carborane 6 gives the 2-metallo derivative in high yields\textsuperscript{145}. Reduction of the resulting metallo derivatives leads to dicarboranylmercury (e.g. 50), typically obtained in high yields\textsuperscript{143,145}. The regioselectivity of mercuration of C-monosubstituted carboranes has not been investigated\textsuperscript{145}.  

Mercuration of monocarbaborate \( \mathbf{2} \) results in the 12-mercurio derivative obtained in 72% yield\(^\text{86} \) and its 1-\( \text{NMe}_3 \) derivative \( \mathbf{51} \) was mercurated to form \( \mathbf{52} \) in 37% yield\(^\text{146} \).

Mercuration of \( \left[ \text{B}_{12}\text{H}_{12} \right]^2- \) gives high yields of dimercurio derivatives, the regiochemistry of which has not been established\(^\text{147} \).

Boron–sulfur bonds. 9-Mercaptocarboranes of ortho- and meta-carboranes have been obtained by direct sulfhydrylation with elemental sulfur in the presence of \( \text{AlCl}_3 \) catalyst in good to excellent yields\(^\text{109,148,149} \). Alternatively, the thiols have been prepared by reaction of carboranes with \( \text{S}_2\text{Cl}_2 \) in the presence of \( \text{AlCl}_3 \), followed by reduction with \( \text{Zn} \) dust and acid or \( \text{NaBH}_4 \) (ref.\(^\text{150} \)).

Reaction of monocarbaborate \( \mathbf{2} \) with dimethyl sulfoxide (DMSO) under acidic conditions leads to the neutral 12-dimethylsulfido derivative isolated in 44% yield along with 23% of a byproduct arising from a DMSO self-condensation reaction\(^67 \). Extending this procedure to cyclic sulfoxide \( \mathbf{53} \) gives about 20% yield of the desired product \( \mathbf{54} \) (ref.\(^\text{151} \)).

A similar reaction of closo-decaborate \( \mathbf{7} \) with DMSO in the presence of HCl yields mixtures of apical and equatorial products\(^\text{133,152} \). Electrophilic sulfurization of closo-dodecaborate \( \mathbf{1} \) with DMSO (ref.\(^\text{153} \)) or (SCN)\(_2 \) (ref.\(^\text{154} \)) results in the almost exclusive formation of the 1,7-isomers, although a small amount of \( \left[ 1,12-(\text{SCN})_2-\text{B}_{12}\text{H}_{10} \right]^2- \) has been isolated\(^\text{154} \).
Other elements bonded to boron. Although B-chloro and B-fluoro derivatives are too unreactive to be useful intermediates in Pd-catalyzed coupling reactions, they can be used to modify the molecular dipole moments\(^{155,156}\) and break the symmetry introducing axial chirality.

A high-pressure carbonylation reaction of the dodecaborate anion 1 gives the highest selectivity among the substitution reactions for the desired 1,12-isomer and dicarbonyl compound 55 was obtained in 40% yield\(^ {157}\). Unfortunately, the difficult reaction conditions needed to form this compound hinder its broader use as the starting material for preparation of other 1,12-disubstituted derivatives of 1.

\[
\begin{align*}
\text{COO} \underbrace{\text{C}}_{55} \underbrace{-2\text{CO}}_{1000\text{ atm}} \underbrace{130^\circ\text{C}}_{\text{Co}_3(\text{CO})_8\text{cat.}} \underbrace{\text{OC}}_{-} \underbrace{-\text{CO}}_{+ \text{other isomers}}
\end{align*}
\]

Reactions of \([\text{B}_{12}\text{H}_{12}]^{2-}\) with other electrophiles proceed with the formation of predominately meta (1,7-) isomers and the desired para (1,12-) isomers are minor products which are difficult to detect and isolate\(^ {132,140,153}\). Similarly, other electrophilic substitution reactions of \([\text{B}_{10}\text{H}_{10}]^{2-}\) yield either mixtures of apical/equatorial or exclusively equatorial\(^6\) products: e.g. reaction with halogens\(^ {158}\), carbonyl chlorides\(^ {132,140,158,159}\), protonated MeCN (ref.\(^ {160}\)), and \(\text{N},\text{N}\)-dimethylthioformamide\(^ {152}\).

**4. FUNCTIONAL GROUP TRANSFORMATIONS**

Several classes of closo-borane derivatives are particularly important intermediates in synthesis of liquid crystalline materials. Among them are carboxylic acids, which are precursors to esters, amines, and nitriles. B-ido derivatives are key intermediates to introduce alkyl, aryl, and acetylene groups. Amines and dinitrogen derivatives of borates 1 and 7 are particularly useful for introduction of onium substituents such as pyridinium and sulfonium. Alkylation and alkylation-cyclization of hydroxy, mercapto, and amino derivatives of boranes are convenient ways to introduce a flexible chain or to build a ring into the molecular rigid core.

Derivatives of closo-boranecarboxylic acids. Formation of esters from carboranecarboxylic acids is typically accomplished in high yield by using carboxylic acid chlorides and an alcohol or phenol in the presence of pyridine or Et\(_3\)N (Scheme 8)\(^ {17,19,20}\). The chlorides of either C- or...
B-carboxylic acids\textsuperscript{48,49} are prepared by using PCl\textsubscript{5}, which is superior to other reagents.

\begin{center}
\begin{tikzpicture}
  \node [draw, shape=rectangle] (a) {R-COOH};
  \node [draw, shape=rectangle, right=of a] (b) {R-COCl};
  \node [draw, shape=rectangle, right=of b] (c) {R'-OH};
  \node [draw, shape=rectangle, below=of a] (d) {R-COO-R'};
  \node [draw, shape=rectangle, below=of b] (e) {R'-alkyl, aryl};
  \node [draw, shape=rectangle, below=of c] (f) {R-NH\textsubscript{2}};

  \draw [->] (a) -- node [above] {PCl\textsubscript{5}} (b);
  \draw [->] (b) -- node [above] {base} (c);
  \draw [->] (c) -- node [above] {1. NaN\textsubscript{3}} (d);
  \draw [->] (d) -- node [above] {2. heat, H\textsubscript{2}SO\textsubscript{4}} (e);
  \draw [->] (e) -- node [above] {} (f);

\end{tikzpicture}
\end{center}

Scheme 8

Carboxylic acids and their anhydride forms (e.g. 55) have been used for the synthesis of amines. For instance, C- and B-carboranecarboxylic acids\textsuperscript{48,49} and also carbonyl derivatives of 1 and 7 undergo a Schmidt-type reaction with H\textsubscript{2}NOSO\textsubscript{3}H in aqueous solution to yield the corresponding amines\textsuperscript{332,157}. A Curtius-type reaction of acid chlorides or anhydrides with NaN\textsubscript{3} leads to the corresponding amines \textsuperscript{87,103,157,161,162} via intermediate isocyanates (Scheme 8)\textsuperscript{157,162}.

Dehydration of carboxamides, conveniently prepared by ammonolysis of carbonyl chlorides\textsuperscript{25}, with trimethylsilyl polyphosphate\textsuperscript{163} provides a high yield route to carboranyl nitriles (e.g. 56)\textsuperscript{96}.

\begin{center}
\begin{tikzpicture}
  \node [draw, shape=rectangle] (a) {H\textsubscript{3}NCO-CONH\textsubscript{2}};
  \node [draw, shape=rectangle, right=of a] (b) {NC-CN};

  \draw [->] (a) -- node [above] {(Me\textsubscript{3}SiOPO\textsubscript{2})\textsubscript{n}} (b);

\end{tikzpicture}
\end{center}

Acid hydrolysis of B-cyanocarboranes furnishes the corresponding carboxylic acids and provides an alternative route to this class of compounds\textsuperscript{51}.

C-Carboranecarbaldehydes such as 57 are susceptible to amine-induced cleavage of the C–C bond as well as cage deboronation (e.g. butylamine). Only the less basic aromatic amines (e.g. aniline) were successfully reacted to form the corresponding Schiff base 58 in good yields\textsuperscript{164}.

\begin{center}
\begin{tikzpicture}
  \node [draw, shape=rectangle] (a) {57};
  \node [draw, shape=rectangle, right=of a] (b) {58};

  \draw [->] (a) -- node [above] {PhNH\textsubscript{2}} (b);

\end{tikzpicture}
\end{center}

Aldehydes, e.g. 57 are most reliably prepared from the corresponding hydroxymethyl derivatives using the Swern oxidation reaction. The hydroxymethyls are typically obtained from reaction of carboranylolithiums and formaldehyde.

\[
\begin{align*}
\text{CHOCH}_2 \text{OH} & \xrightarrow{1. \text{(COCl)}_2, \text{DMSO}} 57 \\
& \xrightarrow{2. \text{Et}_3 \text{N}} 43\%
\end{align*}
\]

Baeyer–Villiger oxidation of closo-borane ketones has not been investigated in detail except in the case of derivatives of \([B_{12}H_{12}]^{2-}\) and \([B_{10}H_{10}]^{-}\), which provide access to the corresponding B-hydroxy derivatives. Other routes to the B-hydroxy compounds include hydrolysis of amide and sulfone adducts to 1 and 7 (ref. 141).

All carborane C-carbonyl compounds including esters, aldehydes, and ketones are susceptible to nucleophile-induced cleavage but are stable under acidic conditions. For the carboranes, the rate of alkaline deformylation follows the order ortho > meta > para. It was demonstrated, however, that basic hydrolysis of ethyl ortho-carborane-1-carboxylate gives excellent yield of the corresponding acid.

Iodo-closo-boranes. A photochemical insertion of \([1.1.1]\)propellane to the C–I bond of 1-iodo-para-carborane (59) to form 60 is a very elegant, and so far the only synthetic application of carborane C–I derivatives. The resulting iodo-bicyclo[1.1.1]pentane derivative 60 was dimerized to form the corresponding [2]staffane derivative in 75% yield.

\[
\begin{align*}
\text{59} & \xrightarrow{\text{hv}} \text{57} \\
\text{60} & \xrightarrow{\text{88\%}}
\end{align*}
\]

B-Iodo compounds undergo Pd-catalyzed cross-coupling reactions with alkyl, aryl, hetaryl, and acetylenyl organometallic reagents. First demonstrated for iodocarboranes, the reaction has also been applied to charged species derived from \([B_{12}H_{11}]^{2-}\) (1) (refs 139,176), \([CB_{11}H_{11}]^{-}\) (2) (ref. 180), and neutral compounds such as ortho-carborane 4 (refs 123,171,173–177,178), meta-carborane 5 (refs 173–175,177,178), and para-carborane 6 (refs 126,175,179). More recently we have used it to transform 41 to 61 (Scheme 9).
Several types of organometallic compounds, including organic derivatives of Mg (refs 123, 126, 171-173, 175-178), Zn (refs 18, 174, 181), and B (ref. 182) have been used and the choice of the metal depends on the iodide structure and the type of organic residue. It was found that in coupling reactions 9-iodo-ortho-carborane is more reactive than the meta isomer177, organozinc reagents are most reactive in the cross-coupling reactions 18, 174, and the reactivity of Grignard reagents can be improved using benzene as the co-solvent177. Cross-coupling reactions of boronic acids with B-iodocarboranes under Suzuki conditions are inefficient giving a large fraction of byproducts 182. Pd(0) catalysts have been found to be more effective than Ni(0) complexes, and the use of CuI as co-catalyst has a beneficial effect on the reaction 126, 173, 180.

Iodide 41 was found to react slowly with alkylzinc reagents in the presence of (PPh3)4Pd and it proved resistant to all coupling reactions performed under other conditions 94. Palladium-catalyzed coupling with either arylboronic esters, alkynes or CuCN failed 94.

B-Iodocarboranes are largely unreactive towards copper-mediated coupling reactions and substitution with thiolate anions 183. 9-iodo-ortho-carborane was converted, however, to the corresponding 9-cyano derivative using CuCN under forcing conditions 184 and it dimerized with copper powder to form 62 (ref. 185).

Carboranyl iodides and other B-halides can be activated towards nucleophilic displacement by converting them into the corresponding
arylcarboranylhalonium salts e.g. 63 (refs.186,187). The reaction has been demonstrated for ortho-, meta-, and para-carboranes and a variety of nucleophiles, and constitutes one the best ways to functionalize the B(9) position in these clusters. The yields are in the range of 11–100% depending on the cluster, halide, aryl substituent, nucleophile and the reaction conditions186.

Amino-closo-boranes. Boranamines are rather weak nucleophiles and their trialkylation requires either a strong electrophile or dipolar aprotic reaction conditions. Generally, alkylation–cyclization of ten-vertex boranamines is easier than that of their twelve-vertex analogs. For instance, amine 64 and diamine 65 were alkylated with tribromide 66 in MeCN and in the presence of Me₄NOH·5H₂O as the base to yield the corresponding 4-pentylquinuclidines 48 and 67, respectively (Scheme 10)16. Similar alkylation of 20
with 66 under the same conditions gave largely HBr elimination products, while using K₂CO₃/18-crown-6 in MeCN allowed isolation of 29% of the quinuclidine 41 (ref. 127).

C-Amino and B-amino groups provide a convenient route to C–S, C–O, and B–F derivatives by diazotization in the presence of the appropriate Lewis base. For instance, the diazotization reaction of 2-amino-meta-carborane 68 in water yields 2-hydroxy-meta-carborane while the same reaction in liquid HF furnishes 83% of 2-fluoro-meta-carborane 48, 49.

\[
\begin{align*}
\text{HNO}_2 / X^- & \quad \text{NH}_2 \\
& \quad \longrightarrow \quad \text{X} \\
& \quad X = \text{F, OH}
\end{align*}
\]

Diazotization of [1-NH₃-CB₁₁H₁₁] (20) (ref. 67) or 1-amino-ortho-carborane 104 in the presence of water or acetic acid yields the corresponding C-hydroxy derivatives in 36% and 60% yield, respectively. Similarly, reaction of 20 (ref. 67) or [1-NH₃-CB₆H₆] (21) (ref. 68) in the presence of dimethyl sulfide furnishes the 1-dimethylsulfido derivatives in about 60% yield. Diazotization of [1-NH₃-CB₁₁H₁₁] (20) in the presence of dimethylthioformamide as the nucleophile allowed for isolation of the corresponding sulfur derivative [1-(SCHNMe₂)-CB₁₁H₁₁] (ref. 151).

\[
\begin{align*}
\text{HNO}_2 & \quad \text{1} = \text{H}_2\text{O, Me}_2\text{S} \\
\text{L} & \quad \text{Me}_2\text{NCHS}
\end{align*}
\]

Reaction of carboranylamines 104 and 1-amino-closo-decaborate (64) 133, 188 with benzaldehyde has been reported to produce the corresponding Schiff bases (e.g. 69) in high yields.

\[
\begin{align*}
\text{Me} & \quad \text{NH}_3 \\
& \quad \longrightarrow \quad \text{PhCHO} \\
& \quad 90% \\
& \quad \text{Me} \\
& \quad \text{N=CH}^{\text{Ph}} \\
& \quad \text{69}
\end{align*}
\]

B-Metallated derivatives. B-Metallo derivatives of closo-boranes such as 70 react with a range of electrophiles under mild conditions, providing access to many important functional groups. Among them are iodides 96, 143 (from I₂),

mercaptans\textsuperscript{189} (from $S_2$), hydroxyls\textsuperscript{190} (from $CrO_3$), and fluorides\textsuperscript{191} (from $BF_3\cdot Et_2O$) obtained either from the mercurio or thallio derivatives.

\begin{center}
\begin{tikzpicture}
  \draw (0,0) circle (1cm);
  \node at (0,0) {\textsuperscript{70}};
  \draw[->] (0,0) -- (1.5,0) node[midway,above] {$M\text{O}_2\text{CCF}_3$};
  \draw[->] (1.5,0) -- (3,0) node[midway,above] {$E = I, SH, OH, F$};
  \draw[->] (3,0) -- (4.5,0) node[midway,above] {$M = Hg, Ti$};
\end{tikzpicture}
\end{center}

The B-mercurio derivatives photodissociate upon irradiation with UV light, and the resulting radicals react with arenes and olefins giving the corresponding B-substitution products in modest to good yields\textsuperscript{144}.

Hydroxy-closo-boranes. The O-anions derived from highly acidic carboranyl OH groups\textsuperscript{115,116} are rather poor nucleophiles and they react well with strong alkylation reagents such as diazomethane\textsuperscript{115}, dimethylsulfate ([1-(OH)$_2$-CB$_{11}$H$_{11}$]) (ref.\textsuperscript{67}), and allyl iodide\textsuperscript{116}. Acid chlorides\textsuperscript{115} and anhydrides\textsuperscript{48,51,192} convert the C-hydroxy\textsuperscript{115} and B-hydroxy\textsuperscript{48,51,192} compounds into corresponding esters in good yields.

An alkylation–cyclization and the formation of the pyran \textsuperscript{71} in good yield has been demonstrated for the [HO-B$_{12}$H$_{11}$]$^2^-$ (ref.\textsuperscript{192}).

\begin{center}
\begin{tikzpicture}
  \draw (0,0) circle (1cm);
  \node at (0,0) {\textsuperscript{71}};
  \draw[->] (0,0) -- (-1.5,0) node[midway,above] {OH};
  \draw[->] (-1.5,0) -- (-3,0) node[midway,above] {Br-(CH$_2$)$_5$-Br};
  \draw[->] (-3,0) -- (-4.5,0) node[midway,above] {KOH in DMSO};
  \draw[->] (-4.5,0) -- (-6,0) node[midway,above] {87\%};
\end{tikzpicture}
\end{center}

Mercapto-closo-boranes. S-Alkylation of either C-thiols\textsuperscript{108,113} or B-thiols\textsuperscript{149,150,193,194} is readily accomplished using moderately reactive electrophiles such as MeI (refs\textsuperscript{108,111,149,150,194}) dimethyl sulfate ([1-(SH)$_2$-CB$_{11}$H$_{11}$]) (ref.\textsuperscript{67}) and alkyl bromides\textsuperscript{113,193}. Alkylation–cyclization of thiolates generated in situ by hydrolysis of thioformamide \textsuperscript{72} with dibromide \textsuperscript{73} gives the corresponding thiacyclohexane derivative \textsuperscript{74} (ref.\textsuperscript{16}).

\begin{center}
\begin{tikzpicture}
  \draw (0,0) circle (1cm);
  \node at (0,0) {\textsuperscript{72}};
  \draw[->] (0,0) -- (-1.5,0) node[midway,above] {SCHNMe$_2$};
  \draw[->] (-1.5,0) -- (-3,0) node[midway,above] {$C_3H_1$-$Br$};
  \draw[->] (-3,0) -- (-4.5,0) node[midway,above] {$C_3H_1$-$Br$};
  \draw[->] (-4.5,0) -- (-6,0) node[midway,above] {Me$_2$NOH+H$_2$O};
  \draw[->] (-6,0) -- (-7.5,0) node[midway,above] {33\%};
\end{tikzpicture}
\end{center}

Oxidation of alkylthio-<sup>149</sup> and arylthiocarboranes<sup>150</sup> with H<sub>2</sub>O<sub>2</sub>–AcOH gives the corresponding sulfoxides and sulfones in excellent yields.

Dinitrogen derivatives of decaborane. Dinitrogen derivatives <sup>44</sup> (ref.131) and <sup>46</sup> (ref.136) provide unique access to a variety of electrically neutral diapical homo- and heterodisubstituted [1-LB<sub>10</sub>H<sub>8</sub>-10-L′] (Scheme 11). Thermal decomposition of the dinitrogen derivatives at temperatures above 100 °C in neat Lewis bases such as substituted pyridine<sup>16,17</sup>, ammonia<sup>16,131</sup>, and N,N-dimethylthioformamide<sup>16,152</sup>, among others<sup>131–133</sup> yields the substitution product. The reaction presumably proceeds through heterolytic cleavage of the B–N bond and the resulting highly energetic intermediate reacts with the available nucleophile, even with benzene and cyclohexane<sup>131</sup>. Therefore the substitution reactions give good and very good yields only for small nucleophiles, but as the hydrocarbon substituents become dominant in the nucleophile molecule (e.g. 4-heptyloxypyridine)<sup>16,17</sup>, the yield diminishes.

Examples of such syntheses are liquid crystals<sup>75–77</sup>, obtained either in a one step process<sup>17</sup> (<sup>75</sup>) or through sequential substitution<sup>16</sup> (<sup>76</sup>, <sup>77</sup>).

Other functional group transformations. Carboranes are relatively resistant to acids and some strong oxidizing reagents and many standard chemical transformations of the side chains and aromatic rings can be accomplished without affecting the carborane ring. It has been found that B-alkyl, -allyl, and -vinyl groups undergo oxidative degradation to form B-COOH acids in high yields<sup>48,49,172,195</sup>. Functionalization of aromatic rings of arylcarboranes have been accomplished by acylation<sup>196</sup>, halogenation<sup>196</sup>, nitration<sup>47,60,123,170,196–198</sup>,...
5. DISCUSSION AND CONCLUSIONS

At first glance, the geometry of closo-boranes resembles that of bicyclo-[2.2.2]octane (BCO): both antipodally disubstituted derivatives have cylindrical rotational symmetry. The BCO ring is considered an important structural element in synthesis of liquid crystal compounds from both fundamental and practical points of view. Most theories of liquid crystal phases assume molecules as cylindrical objects but in reality there are only very few such compounds except for some BCO derivatives. The use of BCO as structural element has also important practical benefits; incorporation of BCO into the molecular structure significantly enhances thermal stability of liquid crystal phases and promotes their nematogenic behavior.

The cylindrical symmetry of the BCO ring is rather rare among the organic rings. Of three such carbocycles (BCO, cubane, and bicyclo-
[1.1.1]pentane) used as structural elements for liquid crystals, BCO is most synthetically available and, based on empirical data, most beneficial for properties. Unfortunately, the chemistry of the BCO ring is rather limited and the substituents must be “built in” during the ring construction (Fig. 3).77

Ten- and twelve-vertex closo-boranes provide an alternative set of “cylindrical” structural elements with different stereochemical and electronic properties. Study of a number and variety of such structurally similar liquid crystalline compounds is an important step towards better understanding the origin of liquid crystallinity. This, however, requires facile functionalization methodology for the rings and access to a variety of chemical structures. In contrast to BCO, parent boron clusters undergo straightforward electrophilic or nucleophilic substitution reactions with typically high regioselectivity ensured by their unusual electronic structures. This also allows for introduction of an off-axis substituent Z which will modify stereochemical and dipolar properties of the material. Very few substituents can be “built in” and NH₂ in 20 and 21 is such an example (vide supra).

During the four decades of development of chemistry of closo-boranes and heteraboranes, an impressive number of organic functional groups have been introduced as substituents. Studies of their chemistry revealed that they undergo typical organic transformations and the clusters generally display reactivity typical of organic compounds rather than of boron hydrides. Further expansion of the “synthetic toolbox” for boron clusters and the availability of a large variety of disubstituted “cylinders” seems straightforward following standard organic-type transformations.

Boron clusters offer much more than an appropriate shape for liquid crystals. Their conformational properties and electronic structures are unique among the ring structures and studies of their effects on liquid crystal behavior have only begun.22,23 Full exploration of these effects will require, however, development of more synthetic and structural chemistry of

![Diagram](image)

Fig. 3
Functionalization of bicyclo[2.2.2]octane (upper line) and closo-boranes (lower line)
the clusters. For instance, methodology for regioselective B(12) substitution of C-monosubstituted ortho-carboranes is almost nonexistent (vide supra) and B(9) substitution of B(2) derivatives of meta-carborane has never been reported. Such compounds would provide access to new liquid crystal structures with variable dipole moments. They could also be used to prepare axially dissymmetric derivatives, which are virtually unknown among the closo-carboranes. A combination of symmetry (or its lack) with the dipole moment is one of the most important issues in basic and applied science of liquid crystals.

Another unexplored area of closo-carborane chemistry is the preparation and functionalization of the B(10) position in monocarbadecaborate (8). In addition, the methods for the preparation of 12-substituted monocarboraborate (2) and 1,12-disubstituted dodecaborate (1) derivatives are still unsatisfactory, and compound 55, currently the best precursor for the latter, is not readily available. All three types of derivatives would give structures with maximally elongated molecular shapes.

Although alkyl and alkylthio substituents have been introduced into boron clusters and their chemistry and stability studied, other groups such as alkoxy, alkylsulfinyl, and alkylsulfonyl are rare. Similarly, the properties of carborane-based azo compounds and Schiff bases is still awaiting more research. Extension of the cylindrical structure of the boranes with quinuclidine and bicyclo[1.1.1]pentane has been reported (vide supra) but coupling with a bridgehead iodide such as 1-iodobicyclo[2.2.2]octane has never been reported.

With time, these and other aspects of chemistry of closo-carboranes will be addressed, bringing more synthetic tools for chemists to engineer new molecular and bulk materials.

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REFERENCES
44. Janoušek Z.: Private communication.


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