**UNCLASSIFIED**

<table>
<thead>
<tr>
<th>AD NUMBER</th>
<th>AD423994</th>
</tr>
</thead>
</table>

**LIMITATION CHANGES**

**TO:**
Approved for public release; distribution is unlimited.

**FROM:**
Distribution authorized to U.S. Gov't. agencies and their contractors;
Administrative/Operational Use; 31 OCT 1963.
Other requests shall be referred to Director, Defense Advanced Research Projects Agency, 3701 North Fairfax Drive, Arlington, VA 22203-1714.

**AUTHORITY**
DARPA ltr 21 Jan 1973
NOTICE: When government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related government procurement operation, the U. S. Government thereby incurs no responsibility, nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.
FIFTH QUARTERLY SUMMARY REPORT

"Mechanism Studies with Boronhydrides"

By M. Frederick Hawthorne
Department of Chemistry
The University of California
Riverside, California

ARPA Order No. 366-62, Amendment No. 1,
ARPA Project Code No. 9100, ARO(D) Project No. 3763-C
For period July 31, 1963 to October 31, 1963
I. **Introduction**

The studies carried out during the Fifth Quarter were mainly concerned with the following topics:

1. Mechanism of $\text{B}_{10}\text{H}_{10}^{-2}$ formation.
2. Mechanism of ligand displacement reactions with $\text{B}_{10}\text{H}_{13}$ (ligand) substrates.
3. Elucidation of the stereo-electronic properties of the $\text{C}_2\text{B}_{10}\text{H}_{11}$ group.

II. **Mechanism of $\text{B}_{10}\text{H}_{10}^{-2}$ Ion Formation**

The work outlined in the Third and Fourth Quarterly Summary Reports has been continued with $\text{B}_{10}\text{H}_{12}(\text{CH}_3\text{CN})(\text{Et}_3\text{N})$ as the reaction substrate. Considerable quantities of $\text{B}_{10}\text{H}_{14}-d_{10}$ have been prepared by the exchange reaction of $\text{B}_{10}\text{H}_{14}$ with DCl in dioxane solution.1

---


This procedure yields $\text{B}_{10}\text{H}_{14}-d_{10}$ with deuterium at the open face of the icosahedral $\text{B}_{10}\text{H}_{14}$ fragment. This isotopically labeled decaborane will be converted to the correspondingly deuterated $\text{B}_{10}\text{H}_{12}(\text{CH}_3\text{CN}) (\text{Et}_3\text{N})-d_8$ derivative by the sequence shown below:

\[
\begin{align*}
\text{B}_{10}\text{H}_4\text{D}_{10} + \text{NaH} & \xrightarrow{25^\circ} \text{NaB}_{10}\text{H}_4\text{D}_9 + \text{HD} \\
\text{NaB}_{10}\text{H}_4\text{D}_9 + \text{Et}_3\text{N} & \xrightarrow{25^\circ} \text{NaB}_{10}\text{H}_4\text{D}_9(\text{Et}_3\text{N}) \\
\text{NaB}_{10}\text{H}_4\text{D}_9(\text{Et}_3\text{N}) + \text{CH}_3\text{CN} + \text{DCl} & \xrightarrow{0^\circ} \text{D}_2 + \text{NaCl} + \text{B}_{10}\text{H}_4\text{D}_8(\text{CH}_3\text{CN})(\text{Et}_3\text{N})
\end{align*}
\]

The substrate $\text{B}_{10}\text{H}_4\text{D}_8(\text{CH}_3\text{CN})(\text{Et}_3\text{N})$ will be examined kinetically with triethylamine in acetonitrile and in benzene solution. If a sizeable primary kinetic isotope appears it may be concluded that...
B-H bond breaking is indeed involved in the second step of the overall reaction sequence which leads to $\text{B}_{10}\text{H}_{10}^2$.

III. **Mechanism of Ligand Displacement Reactions with $\text{B}_{10}\text{H}_{13} (\text{ligand})$ Substrates.**

Work on this problem has recently centered about the optical resolution of the $\text{B}_{10}\text{H}_{13}\text{[N(CH}_2\text{)}(\text{Et})(\text{Me})]}$ anion which contains an asymmetric nitrogen atom. Dissociation of this group during the displacement reaction would lead to racemization at nitrogen. To date only partial resolution has been obtained and optical rotations are too low to permit kinetic experiments.

IV. **Elucidation of the Stereo-Electronic Properties of the $\text{C}_2\text{B}_{10}\text{H}_{11}^-$ Group.**

The nitration of phenylcarborane ($\phi\text{C}_2\text{B}_{10}\text{H}_{11}$) with mixed acid at $80^\circ$ produces a 50:50 mixture of $m$- and $p$-nitrophenylcarboranes. Separation of these isomers followed by catalytic hydrogenation produced the corresponding anilines in quantitative yield. The $m$- and $p$-aminophenylcarboranes will be examined as substrates in representative reactions with known (or easily determined) rho values. In this manner values for the carborane nucleus may be obtained. Further work will involve the determination of the solvolysis rate constants for $m$- and $p$-carboranyl benzyl halides.
UNCLASSIFIED