In a continuation of papers [1, 2] on the preparation and investigation of derivatives of (3)-1,2-dicarbaundecaborate a series of ketones and carboxylic acids, their esters, amides, and nitriles was synthesized in this research containing the 1-(3)-1,2-dicarbaundecaborate substituent and some of their properties were studied.

These compounds were obtained by cleavage of the corresponding derivatives of o-carborane with piperidine [3] in benzene solution and were isolated as the tetramethylammonium salts.

\[
\text{RC} = \text{CR'} + \text{C}_6\text{H}_{10} \text{NH} \xrightarrow{1. \text{C}_6\text{H}_{10} \text{N} \text{O}} \text{RC} = \text{CR'} \\quad \text{B}_9\text{H}_{10} \text{N(C}_6\text{H}_{10})
\]

\[
1. \text{C}_6\text{H}_{10} \text{N} \text{O} \quad \text{B}_9\text{H}_{10} \text{N(C}_6\text{H}_{10}) \quad 2. \text{C}_6\text{H}_{10} \text{N} \text{O} \quad \text{B}_9\text{H}_{10} \text{N(C}_6\text{H}_{10})
\]

\[
\begin{align*}
R = \text{H}, & \quad R' = \text{COOH} \quad \text{(Ia)}; \\
R = \text{CH}_3, & \quad R' = \text{COOCH}_3 \quad \text{(IIa, b)}; \\
R = \text{CH}_3, & \quad R' = \text{CONH}_2 \quad \text{(IV);} \\
R = \text{Cl}, & \quad R' = \text{COOCH}_3 \quad \text{(IIIb);} \\
R = \text{CH}_3, & \quad R' = \text{CN} \quad \text{(V)};
\end{align*}
\]

Compound (V) was obtained by cleavage of 1-methyl-2-cyano-o-carborane with methanol at 20° [4]. Compound (VI) was obtained by the method of [2] by reaction of NaCN and N,N,N,N-trimethylammoniummethyl-(3)-1,2-dicarbaundecaborate.

The structure of the compounds was confirmed by IR spectra (Table 1). In IR spectra of all compounds where the CO or CN group is bonded directly to a (3)-1,2-dicarbaundecaborate grouping a shift of their absorption band to the longwave region is observed, in comparison with the absorption band of the corresponding compound of the carborane series [4-6], which is explained by a difference in electronic effects of the 1-o-carborane and 1-(3)-1,2-dicarbaundecaborate substituent.

It should be noted that alcoholic base cannot be used for cleavage of the indicated derivatives of o-carborane, since cleavage of the C-R bond between the o-carborane ring and the carbonyl group occurs primarily in this case. Even in an attempt to obtain the dicarbaundecaborate secondary alcohol by cleavage of 1-(methyl-o-carboranyl)-2-methyl-1-propanol (VII) under the effect of alcoholic KOH cleavage of the C-C bond between the carborane ring and C atom with the hydroxy group and cleavage of the 1-methyl-o-carborane formed in this case to methyl-(3)-1,2-dicarbaundecaborate occurred initially.

It was shown earlier [7, 8] that the 1-(3)-1,2-dicarbaundecaborate group shows a strong electron-donor effect both by an induction mechanism ($\sigma_L^+ 0.20$) and by a conjugation mechanism ($\sigma_L^0 0.17$). Results obtained in this research on the study of properties of the synthesized derivatives of (3)-1,2-dicarbaundecaborate are in good agreement with these data. The $pK_a$ of acids (Ia)-(Ic) were determined by the method of potentiometric titration in 50% ethanol and 80% methylcellulose. The obtained data are presented in Table 2. Dicarbaundecaborate-carboxylic acids are very strong acids due to the strong electron-donating effect of the 1-(3)-1,2-dicarbaundecaborate group, in contrast to carboranecarboxylic acids. They are much weaker than C$_6$H$_5$COOH [7] and are similar in $pK_a$ to ferrocenecarboxylic acid [9] and p-nitrophenol [10].


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TABLE 1

<table>
<thead>
<tr>
<th>Compound</th>
<th>R</th>
<th>R²</th>
<th>Found, %</th>
<th>Empirical formula</th>
<th>Calc., %</th>
<th>δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Ia)</td>
<td>H</td>
<td>COOH</td>
<td>38.50</td>
<td>9.59</td>
<td>C₂H₅B₆N₄O₅</td>
<td>38.50</td>
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<tr>
<td>(Ib)</td>
<td>H</td>
<td>CH₃COOH</td>
<td>38.50</td>
<td>9.64</td>
<td>C₂H₅B₆N₄O₅</td>
<td>38.50</td>
</tr>
<tr>
<td>(Ic)</td>
<td>CH₃</td>
<td>COOH</td>
<td>38.50</td>
<td>9.56</td>
<td>C₂H₅B₆N₄O₅</td>
<td>38.50</td>
</tr>
<tr>
<td>(IIa)</td>
<td>CH₃</td>
<td>CH₃COOH</td>
<td>38.50</td>
<td>9.56</td>
<td>C₂H₅B₆N₄O₅</td>
<td>38.50</td>
</tr>
<tr>
<td>(IIb)</td>
<td>CH₃</td>
<td>CH₃COCH₃</td>
<td>38.50</td>
<td>9.56</td>
<td>C₂H₅B₆N₄O₅</td>
<td>38.50</td>
</tr>
<tr>
<td>(IIc)</td>
<td>CH₃</td>
<td>CH₃CN</td>
<td>38.50</td>
<td>9.56</td>
<td>C₂H₅B₆N₄O₅</td>
<td>38.50</td>
</tr>
<tr>
<td>(IIId)</td>
<td>CH₃</td>
<td>CN</td>
<td>38.50</td>
<td>9.56</td>
<td>C₂H₅B₆N₄O₅</td>
<td>38.50</td>
</tr>
</tbody>
</table>

* Tetraethylammonium salt.

TABLE 2

<table>
<thead>
<tr>
<th>Formula</th>
<th>pKₐ</th>
<th>90% methanol</th>
<th>50% methanol</th>
<th>90% methylcellosolve</th>
<th>50% ethanol</th>
<th>90% methylcellosolve</th>
</tr>
</thead>
<tbody>
<tr>
<td>HC=CCOOH</td>
<td>7,13</td>
<td>8,97</td>
<td>2,50</td>
<td>6,96</td>
<td>7,66</td>
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<tr>
<td>Bu₃H₁₀⁺N(CH₃)₄</td>
<td></td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>CH₃C=CCOOH</td>
<td>7,31</td>
<td>9,10</td>
<td>2,60</td>
<td>8,08</td>
<td>7,56</td>
<td></td>
</tr>
<tr>
<td>Bu₃H₁₀⁺N(CH₃)₄</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HC=CCH₂COOH</td>
<td>8,92</td>
<td>8,38</td>
<td>4,23</td>
<td>6,20</td>
<td>7,89</td>
<td></td>
</tr>
<tr>
<td>Bu₃H₁₀⁺N(CH₃)₄</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Acids (Ia)-(Ic) are monosalts of dibasic acids containing two acidic groups: carboxyl and nido-(3)-1,2-dicarbaundecaborate. Since the acidity of nido-(3)-1,2-C₃B₆H₁₂ dicarbaundecaborane (pKₐ 2.95 in 33% methanol) is four orders of magnitude higher than the acidity of the carboxyl group [11], acids (Ia)-(Ic) are ammonium salts of (3)-1,2-C₃B₆H₁₂, which is seen from their IR spectra.

The induction constant of 1-(3)-1,2-C₃B₆H₁₂ is 0.26 was calculated using the pKₐ value of acid (Ib) in 80% methylcellosolve by the method of [12]. This value is close to the value 0.20 calculated by the Taft method [7, 8].

In contrast to o-carboranecarboxylic esters [5], ketones [4], and secondary alcohols [4], which upon reaction with alcoholic base easily undergo cleavage of the C-C bond between the o-carborane ring and the organic substituent, the corresponding derivatives of (3)-1,2-dicarbaundecaborate were stable to the effect of alcoholic KOH even under rigid conditions. This result agrees with the character of the electronic effect of the 1-(3)-1,2-dicarbaundecaborate group, and also shows that formation of an anionic center at the carbon atom of (3)-1,2-dicarbaundecaborate is extremely inconvenient.

Transformation of the CO group to CH₂ group with formation of the benzyl derivative (VIII) can occur upon reaction of ketone (IIa) with excess LiAlH₄ in THF solution.

\[
\begin{align*}
\text{CH₃C–CCOOH} & \xrightarrow{\text{LiAlH₄}} \text{CH₃C–CCH₂COOH} \\
\text{Bu₃H₁₀⁺N(CH₃)₄} & \text{Bu₃H₁₀⁺N(CH₃)₄} \\
\text{CH₃C–CCH₂COOH} & \xrightarrow{-\text{OH}^-} \text{CH₃C–CCOOH} \\
\text{Bu₃H₁₀⁺N(CH₃)₄} & \text{Bu₃H₁₀⁺N(CH₃)₄} \\
\end{align*}
\]

(VIII)

A mixture of phenyl(methyldicarbaundecarboranyl)carbinol (IX) and benzyl derivative (VIII) in a 2:3 ratio is obtained already 15 min after the start of reaction. Reduction of the ketone to compound (VIII) occurs even at -30°C. At -30°C after 15 min the reaction solution is a mixture of initial ketone, compounds (IX), and (VIII) in a 2.1:1.7:1 ratio, which indicates the similarity of rates of reduction of the keto group of ketone (IIia) to the alcohol