POLYNUCLEAR BORANE ANIONS AS MILD REDUCING AGENTS

1. THE OCTAHYDROTRIBORATE(1-) ANION

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Tetra-n-butylammonium octahydrotriborate(1-) in chloroform is a convenient, mild reagent for reduction of aromatic and aliphatic ketones, aldehydes and acid chlorides.

Although the tetrahydroborate(1-) ion and its derivatives have found extensive use in organic and organometallic syntheses,1-9 the octahydrotriborate(1-) ion has been utilized solely for the preparation of higher boranes, polyhedral borane anions, and transition metal complexes.10-14 $\text{B}_3\text{H}_8^-$ can be conveniently prepared in the form of a variety of air stable, non-hygrosopic salts which are soluble in a wide range of protic and aprotic solvents.13 We wish to report the first use of tetra-n-butylammonium octahydrotriborate(1-), $[\text{n-But}_4\text{N}][\text{B}_3\text{H}_8]$, as a mild reducing agent for the conversion of a variety of aromatic and aliphatic ketones, aldehydes and acid chlorides to their corresponding alcohols.

A typical procedure is represented in equation (1). Freshly distilled benzaldehyde (0.229 g, 2.16 mmol) and $[\text{n-But}_4\text{N}][\text{B}_3\text{H}_8]$ (0.178 g, 0.63 mmol) were combined in 10 cc HCCl$_3$ and stirred at reflux for 20 hrs. Dibenzyl ether was added as an internal standard, and the resulting solution was washed with 10% HCl and saturated NaHCO$_3$, dried with MgSO$_4$ and concentrated for glc analysis.

$$\text{C}_6\text{H}_5\text{CH} + [\text{n-But}_4\text{N}][\text{B}_3\text{H}_8] \xrightarrow{(1) \text{HCCl}_3/\text{reflux} / 20 \text{ hr}} \text{C}_6\text{H}_5\text{CH}_2\text{OH} \quad (1)$$

2.16 mmol 0.63 mmol

1.91 mmol

(88.4 %)
Table I. Yields of Alcohols Produced by [n-But₄N][B₃H₈] Reductions of Carbonyl Compounds

<table>
<thead>
<tr>
<th>Entry</th>
<th>Carbonyl Compound</th>
<th>Solvent</th>
<th>Alcohol Product</th>
<th>Yield (%)²</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Benzaldehyde</td>
<td>HCl</td>
<td>Benzylic Alcohol</td>
<td>94.0</td>
</tr>
<tr>
<td>2.</td>
<td>&quot;</td>
<td>CH₃CN</td>
<td>&quot;</td>
<td>86.0</td>
</tr>
<tr>
<td>3.</td>
<td>&quot;</td>
<td>CH₃OH</td>
<td>&quot;</td>
<td>99.2</td>
</tr>
<tr>
<td>4.</td>
<td>2-Chlorobenzaldehyde</td>
<td>HCl</td>
<td>2-Chlorobenzylic Alcohol</td>
<td>83.9</td>
</tr>
<tr>
<td>5.</td>
<td>Hexanal</td>
<td>&quot;</td>
<td>1-Hexanol</td>
<td>66.6</td>
</tr>
<tr>
<td>6.</td>
<td>Heptanal</td>
<td>&quot;</td>
<td>1-Heptanol</td>
<td>84.0</td>
</tr>
<tr>
<td>7.</td>
<td>Cyclohexanone</td>
<td>&quot;</td>
<td>Cyclohexanol</td>
<td>90.8</td>
</tr>
<tr>
<td>8.</td>
<td>&quot;</td>
<td>CH₃OH</td>
<td>&quot;</td>
<td>90.7</td>
</tr>
<tr>
<td>9.</td>
<td>Cyclopentanone</td>
<td>HCl</td>
<td>Cyclopentanol</td>
<td>78.1</td>
</tr>
<tr>
<td>10.</td>
<td>2-Methylcyclohexanone</td>
<td>&quot;</td>
<td>2-Methylcyclohexanol</td>
<td>86.6</td>
</tr>
<tr>
<td>11.</td>
<td>3-Methylcyclohexanone</td>
<td>&quot;</td>
<td>3-Methylcyclohexanol</td>
<td>95.4</td>
</tr>
<tr>
<td>12.</td>
<td>2-Pentanone</td>
<td>&quot;</td>
<td>2-Pentanol</td>
<td>80.2</td>
</tr>
<tr>
<td>13.</td>
<td>2-Octanone</td>
<td>&quot;</td>
<td>2-Octanol</td>
<td>98.8</td>
</tr>
<tr>
<td>14.</td>
<td>Acetophenone</td>
<td>&quot;</td>
<td>I-Phenylethanol</td>
<td>98.2</td>
</tr>
<tr>
<td>15.</td>
<td>Benzoyl Chloride</td>
<td>&quot;</td>
<td>Benzylic Alcohol</td>
<td>83.8</td>
</tr>
<tr>
<td>16.</td>
<td>Hexanoyl Chloride</td>
<td>&quot;</td>
<td>1-Hexanol</td>
<td>73.5</td>
</tr>
</tbody>
</table>

²G.L.C. yields are averages of at least two separate reactions. G.L.C. conditions: 6' x 1/8" 10% Carbowax 20M on Chromasorb W; products identified by standard spectral analyses. ²Based upon mmoles of carbonyl compound.

Table I describes the yields of alcohols obtained when a representative series of carbonyl compounds was reacted with [n-But₄N][B₃H₈]. Moderate to excellent yields are obtained from aliphatic and aromatic acid chlorides; aldehydes and ketones. Results for benzaldehyde and cyclohexanone indicate excellent yields can be obtained using a variety of protic and aprotic solvents. However, HCl was found to be most generally useful, particularly for reductions of the less reactive ketones. B₃H₈⁻ undergoes significant solvolytic decomposition in methanol during the reaction periods required for complete reduction of 2-octanone and acetophenone.

The stoichiometric ratio of B₃H₈⁻ to carbonyl compound varies from 1:1 for reduction of acid chlorides to 1:3 for aldehydes and ketones. In order to determine the maximum number of hydrogens available for such reductions, a sample of [n-But₄N][B₃H₈] was suspended in distilled water and analyzed gasometrically by the H₂ evolution method. Addition of excess 6N HCl generated exactly 8.0 mmols H₂ per mmole B₃H₈⁻. This determination indicates that indeed a maximum of eight hydrogens can be transferred under
appropriate reaction conditions. Current efforts are directed at increasing the number of hydrogens transferred during carbonyl reductions.

IR spectra of a reaction mixture containing benzaldehyde (2.19 mmol) and [n-But₄N][B₃H₈] (0.70 mmol) in 5 cc refluxing HCCl₃ were recorded as a function of time and indicated the smooth disappearance of the aldehydic C-H and C=O absorptions. At completion these bands were not detectable and there was no evidence of an O-H stretch. It is noteworthy that during reaction there occurred a smooth increase in absorptions at 1330 cm⁻¹ and 1060 cm⁻¹ associated with the formation of B-O and C-O bonds, respectively. At the end of reaction the mixture was completely hydrolyzed using 10% HCl. The IR spectrum of the isolated product indicated complete conversion of benzaldehyde to benzyl alcohol. These results demonstrate that [n-But₄N][B₃H₈] reacts with benzaldehyde (and carbonyl compounds in general) to produce an alkylborate which, when treated with dilute aqueous acid, yields the corresponding alcohol. The B-H stretching absorptions at 2420 and 2110 cm⁻¹ smoothly decreased, but throughout reaction their positions and relative intensities remained unchanged. In addition, no new B-H absorptions appeared. Results from the IR study taken together with the stoichiometries obtained in reactions of [n-But₄N][B₃H₈] with carbonyl compounds suggest that the triangular B₃ framework of the reducing agent is maintained throughout the reaction and that the alkylborate product can be formulated as B₃H₈-x(OR)x.

Preliminary relative rate studies indicate the following general order of substrate reactivity:

\[
\begin{align*}
\text{RCCl} & > \text{RCH} > (\text{CH}_2)_n\text{C}=\text{O} > \text{RCR}' \\
\text{1} & : 0.2 : 0.1 : 0.025
\end{align*}
\]

This is typical of the order expected for the reaction of carbonyl compounds with hydridic nucleophiles. In addition, the trend in relative rates is in good agreement with values obtained for reactions of NaBH₄ in dioxane and isopropyl alcohol. These data suggest the possibility for selective acid halide or aldehyde reduction in the presence of various ketone functionalities. Chemoselectivity studies are currently being investigated.
References