

## 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,<sup>1-9</sup> the octahydrotriborate(1-) ion has been utilized solely for the preparation of higher boranes, polyhedral borane anions, and transition metal complexes.<sup>10-14</sup>  $B_3H_8^-$  can be conveniently prepared in the form of a variety of air stable, non-hygroscopic salts which are soluble in a wide range of protic and aprotic solvents.<sup>13</sup> We wish to report the first use of tetra-*n*-butylammonium octahydrotriborate(1-),  $[n\text{-But}_4N][B_3H_8]$ , 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  $[n\text{-But}_4N][B_3H_8]$  (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.

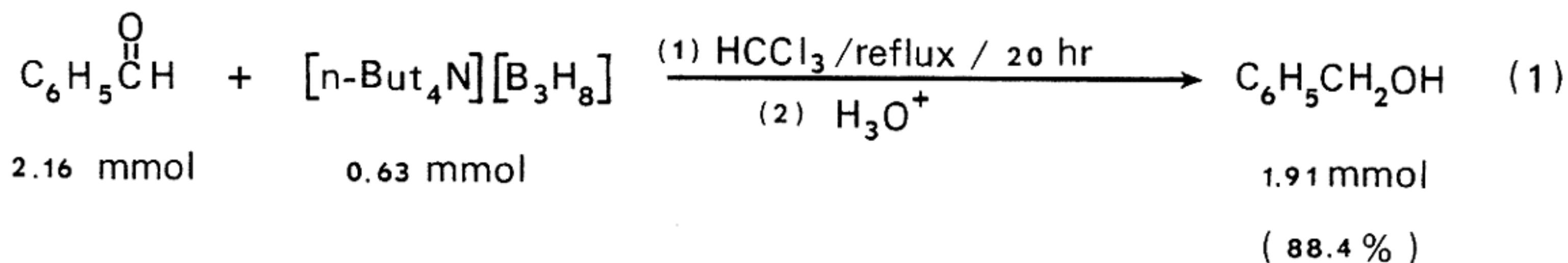


Table I. Yields of Alcohols Produced by [n-But<sub>4</sub>N][B<sub>3</sub>H<sub>8</sub>] Reductions of Carbonyl Compounds<sup>a</sup>

Entry	Carbonyl Compound	Solvent	Alcohol Product	Yield (%) <sup>b</sup>
1.	Benzaldehyde	HCCl <sub>3</sub>	Benzyl Alcohol	94.0
2.	"	CH <sub>3</sub> CN	"	86.0
3.	"	CH <sub>3</sub> OH	"	99.2
4.	2-Chlorobenzaldehyde	HCCl <sub>3</sub>	2-Chlorobenzyl Alcohol	83.9
5.	Hexanal	"	1-Hexanol	66.6
6.	Heptanal	"	1-Heptanol	84.0
7.	Cyclohexanone	"	Cyclohexanol	90.8
8.	"	CH <sub>3</sub> OH	"	90.7
9.	Cyclopentanone	HCCl <sub>3</sub>	Cyclopentanol	78.1
10.	2-Methylcyclohexanone	"	2-Methylcyclohexanol	86.6
11.	3-Methylcyclohexanone	"	3-Methylcyclohexanol	95.4
12.	2-Pentanone	"	2-Pentanol	80.2
13.	2-Octanone	"	2-Octanol	98.8
14.	Acetophenone	"	1-Phenylethanol	98.2
15.	Benzoyl Chloride	"	Benzyl Alcohol	83.8
16.	Hexanoyl Chloride	"	1-Hexanol	73.5

<sup>a</sup>G.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. <sup>b</sup>Based upon mmoles of carbonyl compound.

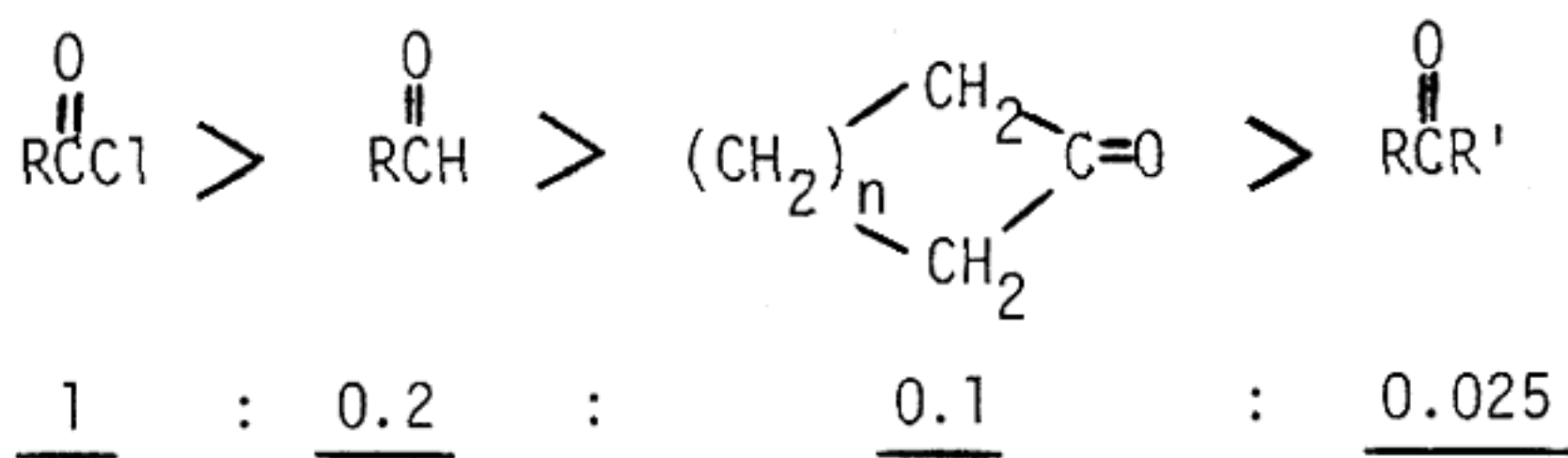
Table I describes the yields of alcohols obtained when a representative series of carbonyl compounds was reacted with [n-But<sub>4</sub>N][B<sub>3</sub>H<sub>8</sub>]. Moderate to excellent yields are obtained from aliphatic and aromatic acid chlorides, aldehydes and ketones. Results for benzaldehyde and cyclohexanone indicate excellent yields can be obtained using a variety of protic and aprotic solvents. However, HCCl<sub>3</sub> was found to be most generally useful, particularly for reductions of the less reactive ketones. B<sub>3</sub>H<sub>8</sub><sup>-</sup> undergoes significant solvolytic decomposition in methanol during the reaction periods required for complete reduction of 2-octanone and acetophenone.

The stoichiometric ratio of B<sub>3</sub>H<sub>8</sub><sup>-</sup> 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-But<sub>4</sub>N][B<sub>3</sub>H<sub>8</sub>] was suspended in distilled water and analyzed gasometrically by the H<sub>2</sub> evolution method.<sup>15</sup> Addition of excess 6N HCl generated exactly 8.0 mmoles H<sub>2</sub> per mmole B<sub>3</sub>H<sub>8</sub><sup>-</sup>. 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  $[n\text{-But}_4\text{N}][\text{B}_3\text{H}_8]$  (0.70 mmol) in 5 cc refluxing  $\text{HCCl}_3$  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  $1330\text{ cm}^{-1}$  and  $1060\text{ cm}^{-1}$  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  $[n\text{-But}_4\text{N}][\text{B}_3\text{H}_8]$  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  $2110\text{ cm}^{-1}$  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  $[n\text{-But}_4\text{N}][\text{B}_3\text{H}_8]$  with carbonyl compounds suggest that the triangular  $\text{B}_3$  framework of the reducing agent is maintained throughout the reaction and that the alkylborate product can be formulated as  $\text{B}_3\text{H}_{8-x}(\text{OR})_x$ .

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



This is typical of the order expected for the reaction of carbonyl compounds with hydridic nucleophiles.<sup>2</sup> In addition, the trend in relative rates is in good agreement with values obtained for reactions of  $\text{NaBH}_4$  in dioxane<sup>16</sup> and isopropyl alcohol.<sup>17</sup> 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.

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