Tetrahedron Letters,Vol.23,No.33,pp 3337-3340,1982 0040-4039/82/333337-04$03.00/0
Printed in Great Britain

POLYNUCLEAR BORANE ANIONS AS MILD REDUCING AGENTS
1 THE OCTAHYDROTRIBORATE(1-) ANION

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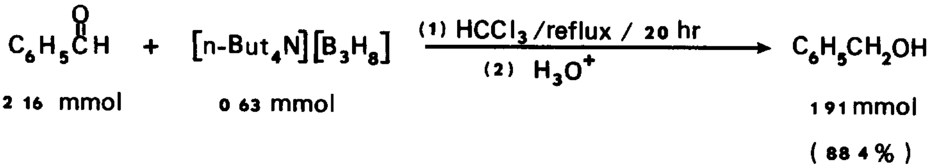
Tetra-n-butylammonium octahydrotriborate(1-) in chloroform is a convenient, mild reagent for reduction of aromatic and aliphatic ketones, aldehydes and acid chlorides

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] $B_3H_8^-$ 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 [13] 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



$$C_6H_5\overset{\overset{O}{\|}}{C}H + [n\text{-}But_4N][B_3H_8] \xrightarrow[(2)\ H_3O^+]{(1)\ HCCl_3/\text{reflux}/20\text{ hr}} C_6H_5CH_2OH \qquad (1)$$

2 16 mmol 0 63 mmol 1 91 mmol
(88 4 %)

Table I Yields of Alcohols Produced by $[n\text{-But}_4N][B_3H_8]$ Reductions of Carbonyl Compounds[a]

Entry	Carbonyl Compound	Solvent	Alcohol Product	Yield (%)[b]
1	Benzaldehyde	$HCCl_3$	Benzyl Alcohol	94 0
2	"	CH_3CN	"	86 0
3	"	CH_3OH	"	99.2
4	2-Chlorobenzaldehyde	$HCCl_3$	2-Chlorobenzyl Alcohol	83 9
5	Hexanal	"	1-Hexanol	66 6
6	Heptanal	"	1-Heptanol	84 0
7	Cyclohexanone	"	Cyclohexanol	90 8
8	"	CH_3OH	"	90.7
9	Cyclopentanone	$HCCl_3$	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

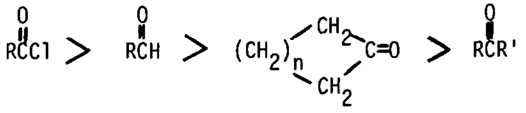
[a] G.L C. yields are averages of at least two separate reactions G L C conditions 6' x 1/8" 10% Carbowax 20M on Chromasorb W, products identified by standard spectral analyses [b] Based upon mmoles of carbonyl compound

Table I describes the yields of alcohols obtained when a representative series of carbonyl compounds was reacted with $[n\text{-But}_4N][B_3H_8]$ 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, $HCCl_3$ was found to be most generally useful, particularly for reductions of the less reactive ketones $B_3H_8^-$ undergoes significant solvolytic decomposition in methanol during the reaction periods required for complete reduction of 2-octanone and acetophenone

The stoichiometric ratio of $B_3H_8^-$ 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 $[n\text{-But}_4N][B_3H_8]$ was suspended in distilled water and analyzed gasometrically by the H_2 evolution method[15] Addition of excess 6N HCl generated exactly 8 0 mmoles H_2 per mmole $B_3H_8^-$ 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 $[n\text{-But}_4N][B_3H_8]$ (0 70 mmol) in 5 cc refluxing $HCCl_3$ were recorded as a function of time and indicated the smooth disappearance of the aldehydic C-H and C=0 absorptions At completion these bands were not detectable and there was no evidence of an 0-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-0 and C-0 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 $[n\text{-But}_4N][B_3H_8]$ 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 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 $[n\text{-But}_4N[[B_3H_8]$ with carbonyl compounds suggest that the triangular B_3 framework of the reducing agent is maintained throughout the reaction and that the alkylborate product can be formulated as $B_3H_{8-X}(OR)_X$

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



1 0 2 0.1 0 025

This is typical of the order expected for the reaction of carbonyl compounds with hydridic nucleophiles [2] In addition, the trend in relative rates is in good agreement with values obtained for reactions of $NaBH_4$ in dioxane[16] and isopropyl alcohol [17] 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

Acknowledgement

This research was supported by a grant from Research Corporation

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(Received in USA 20 May 1982)