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POLYNUCLEAR BORANE ANIONS AS MILD REDUCING AGENTS
2. THE OCTAHYDROTRIBORATE (1-) ANION IN THE PRESENCE OF PROMOTERS

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Abstract: A variety of metal compounds are shown to be effective promoters for the tetra-n-butylammonium octahydrotriborate (1-) reduction of carbonyl compounds in THF at room temperature.

The versatility of boron hydride reducing agents can be greatly increased by combination with a variety of metal complexes. $NaBH_4$ systems have been especially well studied: lanthanide salts promote exclusive carbonyl reduction in $NaBH_4$ reactions with α-enones[1]; $NaBH_4$ in the presence of $TiCl_4$, $SnCl_4$ or the combination of dioxygen and catalytic amounts of octaethylporphinatorhodium(III) chloride is highly effective for conversion of alkenes to alcohols via antimarkownikoff addition;[2-4] $NaBH_4$ combined with cobalt(II) salts reduces alkenes and alkynes to alkanes;[5] and tris-(triphenylphosphine)nickel(0) catalyzes $NaBH_4$ hydrogenolysis of aromatic bromides.[6] In general, these procedures include the use of large excesses of $NaBH_4$ and reduction is accompanied by substantial H_2 evolution.

We recently reported 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.[7] Although reduction proceeds smoothly in chloroform, solutions containing carbonyl compounds and $[n\text{-}But_4N][B_3H_8]$ in refluxing THF showed no evidence of reaction for periods greater than 100 hrs. We wish to report the identification of a variety of metal complexes which act as efficient promoters for reductions in THF. These promoters affect both the rate and stereochemistry of $B_3H_8^-$ reductions.

$[n\text{-}But_4N][B_3H_8]$ in THF at room temperature reacts rapidly and completely with a variety of metal complexes to produce H_2 and, in a few cases, finely divided metal. The reaction stoichiometry, in the presence of cyclohexanone, was determined by IR spectral titration. In a typical experiment cyclohexanone (0.203 g, 2.07 mmol) and $[But_4N][B_3H_8]$ (0.072 g, 0.253 mmol) were weighed into a 50 cc flask and dissolved in 5.0 cc THF. After stirring 15 min, the IR spectrum (2600-1500 cm^{-1}) was recorded using the absorbance mode. Zinc nitrate (0.019 g, 0.065 mmol) was added. The mixture was stirred for 15 min, and the absorbance spectrum was again recorded. Zinc nitrate additions were repeated until the B-H absorbance (2434 cm^{-1}) reached zero and there was no further change in carbonyl absorbance (1714 cm^{-1}).

Table I contains spectral titration results presented as the stoichiometric reduction ratio (mmol cyclohexanone/mmol $B_3H_8^-$) for a variety of promoters. Although there is a wide range in promoter efficiency, certain generalities are evident: simple salts are more effective than neutral carbonyl compounds, anhydrous and hydrated salts are equally effective, the

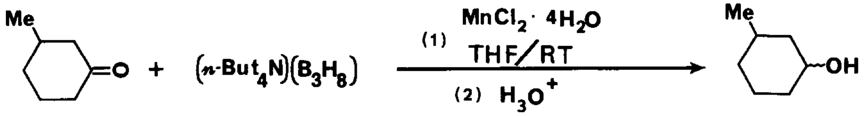
Table I. $[n\text{-}But_4N][B_3H_8]$ Reduction Stoichiometries from IR Spectral Titrations[a].

Entry	Promoter	mmol Cyclohexanone Reduced/mmol $[n\text{-}But_4N][B_3H_8]$
1	$CrCl_3 \cdot 6H_2O$	5.8
2	$MnCl_2 \cdot 4H_2O$	7.8
3	$FeCl_3 \cdot 6H_2O$	3.2
4	$CuCl_2$ x H_2O	2.6
5	CuCl	1.8
6	$ZnCl_2$, $[Zn(NO_3)_2 \cdot 6H_2O]$	5.0 [5.2]
7	$Cd(NO_3)_2 \cdot 4H_2O$	5.3
8	HgI_2	6.8
9	$Fe_2(CO)_9$	1.2
10	$Co_2(CO)_8$	2.6
11	$LaCl_3 \cdot 6H_2O$	5.2

[a] Averages from at least two separate reactions. Good Beer's Law plots were obtained for $[n\text{-}But_4N][B_3H_8]$ and cyclohexanone in THF. Standard deviation of mean values of stoichiometric ratio (± 0.1).

reduction ratio is independent of the anion, metals in lower oxidation states give poorer reduction ratios, and metal ions generally considered powerful Lewis acids give the highest reduction ratios. In addition, $MnCl_2 \cdot 4H_2O$ is identified as the most effective promoter in the series.

Aromatic and aliphatic ketones, aldehydes and acid chlorides are rapidly reduced by $[n\text{-}But_4N][B_3H_8]$ in combination with $MnCl_2 \cdot 4H_2O$. A typical procedure is represented in equation (1).



(1)

2.03 mmol 0.308 mmol 1.97 mmol (96.7%)

3-methylcyclohexanone (0.2281 g, 2.03 mmol) and $[n\text{-}But_4N][B_3H_8]$ (0.0872 g, 0.308 mmol) were combined in 10 cc THF. $MnCl_2 \cdot 4H_2O$ (0.1424 g, 0.720 mmol) was gradually added until no B-H IR absorptions were detectable. Reaction was usually complete within 10 minutes, after which dibenzyl ether was added as internal standard. The resulting solution was combined with diethyl ether, washed with 10% HCl and sat'd $NaHCO_3$, dried with $MgSO_4$ and concentrated for GLC analysis. Table II presents results for $MnCl_2 \cdot 4H_2O$ promoted reductions. In general, yields range from high for ketones and benzaldehyde to moderate for acid chlorides and heptanal.

Table III presents results for the reduction of 3,3,5-trimethylcyclohexanone in 10 cc THF at RT in the presence of the full series of promoters from Table I. Although there is a wide variation in alcohol yield which reflects the activity of the individual promoter, the small

Table II. Alcohol Yields from $MnCl_2 \cdot 4H_2O$ Promoted $[n\text{-}But_4N][B_3H_8]$ Reductions.[a]

Entry	Carbonyl Compound	Alcohol Product	Yield (%)[b]
1	Benzaldehyde	Benzyl Alcohol	87.6
2	Heptanal	1-Heptanol	43.1
3	Cyclohexanone	Cyclohexanol	83.0
4	3-Methylcyclohexanone	3-Methylcyclohexanol	92.6
5	2-Octanone	2-Octanol	99.4
6	Acetophenone	1-Phenylethanol	99.6
7	Benzoyl Chloride	Benzyl Alcohol	65.4
8	Hexanoyl Chloride	1-Hexanol	60.6

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

Table III. Effect of Promoters on $[But_4N][B_3H_8]$ Reduction of 3,3,5-Trimethylcyclohexanone.[a]

Entry	Promoter	Promoter/$B_3H_8^-$ (mmol ratio)	3,3,5-Trimethylcyclohexanol	
			Yield (%)[b]	Trans (%)[c]
1	$CrCl_3 \cdot 6H_2O$	0.76	45.7	87.6 (±1.0)
2	$MnCl_2 \cdot 4H_2O$	1.00	56.2	76.7 (±2.3)
3	$FeCl_3 \cdot 6H_2O$	0.50	62.2	65.0 (±0.0)
4	$CuCl_2$ x H_2O	0.62	54.7	87.9 (±0.1)
5	CuCl	2.00	72.9	79.0 (±1.2)
6	$ZnCl_2$	1.00	85.6	84.2 (±0.2)
7	$Cd(NO_3)_2 \cdot 4H_2O$	2.00	15.2	85.4 (±0.8)
8	HgI_2	0.50	100	82.0 (±0.2)
9	$Fe_2(CO)_9$	2.00	95.0	76.3 (±0.7)
10	$Co_2(CO)_8$	0.50	99.2	85.1 (±0.4)
11	$LaCl_3 \cdot 6H_2O$	1.00	96.0	57.8 (±0.23)
12	None[d]		74.6	85.0 (±2.8)

[a] GLC yields are averages of at least two separate reactions. GLC conditions: glass 6' x 1/8" 10% EGA on Chrom W. [b] Based on 2.02(±0.05) mmol ketone and 1.00(±0.01) mmol $[But_4N][B_3H_8]$ in 10 cc THF at RT. [c] GLC area ratio. [d] Performed in refluxing $HCCl_3$[7].

range of stereoselectivities (76.3-87.9% trans) agrees well with the value obtained in the absence of promoter (entry 12). Notable exceptions are the strong Lewis acids Fe(III) and La(III) which promote enhanced cis-selectivity. Independent experiments indicate that these ions in the presence of dilute HCl do not epimerize 3,3,5-trimethylcyclohexanol.

To date our understanding of the role of metal promoters in $B_3H_8^-$ reductions is incomplete; however, the availability of between 5 and 8 hydrogens for carbonyl reductions represents a significant improvement over nonpromoted reactions.[7]

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References

1. A.L. Gemal and J.L. Luche, J. Amer. Chem. Soc., 103, 5454(1981).
2. S. Kano, Y. Tanaka, and S. Hibino, J. Chem. Soc., Chem. Commun., 414(1980).
3. S. Kano, Y. Yuasa and S. Shibuya, J. Chem. Soc., Chem. Commun., 796(1979).
4. Y. Aoyama, T. Watanabe, H. Onda and H. Ogoshi, Tetrahedron Lett., 24, 1183(1983).
5. S.K. Chung, J. Org. Chem., 44, 1014(1979).
6. S.T. Lin and J.A. Roth, J. Org. Chem., 44, 309(1979).
7. W.H. Tamblyn, D.H. Weingold, E.D. Snell and R.E. Waltermire, Tetrahedron Lett., 23, 3337

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