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CATECHOLBORANE (1,3,2-BENZODIOXABOROLE) AS A VERSATILE REDUCING AGENT

A Dissertation

Presented for the

Doctor of Philosophy

Degree

The University of Tennessee, Knoxville

John Dayton Baker, Jr.

June 1978

1361731

DEDICATION

The author wishes to dedicate this work most of all to Joanna and to his parents Helen, John, Woodrow, Reba, Noel, Dayton, Mable, Saford, and Adeline, to his brothers Raymond and Bobby, to his sister Dorothy, to his aunts, uncles, cousins, friends, Dr. David Beck, and to the family of mankind.

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The author is deeply grateful to those at The University of Tennessee whose dedication and enthusiasm make them some of the finest authors and educators in their field.

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ABSTRACT

The chemistry of 1,3,2-benzodioxaborole [catecholborane (CB)] was investigated. CB was found to be a selective reducing agent. CB reduced the following functional groups rapidly (24 hr or less): aldehyde, hydrazone, acid salt, sulfoxide, amine oxide, anhydride, epoxide, alkyne, acetal, and ketal. CB reduced the following functional groups slowly (greater than 24 hr): ketone, acid chloride, terminal alkene, nitrile, acid, and tertiary amide. CB was inert toward the following: ester, disulfide, nitro, sulfone, internal alkene, lactone, alkyl bromide, and alkyl iodide.

Tosylhydrazones were reduced rapidly by CB. Reaction of a tosylhydrazone with CB and subsequent decomposition using sodium acetate trihydrate gave the corresponding methyl or methylene derivatives in good yields. The tosylhydrazones of α,β-unsaturated ketones and aldehydes gave alkenes in which the double bond had rearranged in a predictable fashion.

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CHAPTER I

INTRODUCTION

Selective reductions are quite important in the field of organic chemistry as evidenced by the large number of selective reducing agents which have been reported in recent years. A selective reduction, strictly speaking, is the preferred reduction of one functional group in the presence of one or more functional groups.

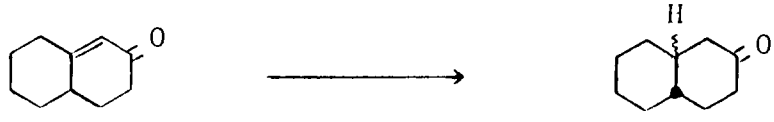
The selective reducing agents reported to date involve a wide variety of chemical reagents and methods. Some of the commonly employed reducing agents and methods are: transition metal hydrides, heterogeneous metal-catalyzed hydrogenations, triphenyltin hydride, zirconium hydride complexes, borane complexes, lithium aluminum hydride and its derivatives, and sodium borohydride and its derivatives.

Complex metal hydrides of various transition metals have been used for selective reductions [1]. For example, the catalytic activity of rhodium complexes in the hydrogenation of olefins is believed to be derived from displacement of loosely coordinated solvent by the olefin moiety followed by a hydride transfer from catalyst to olefin. Using a rhodium complex, the selective reduction of a dieneone can be accomplished (Eq. 1) [2].



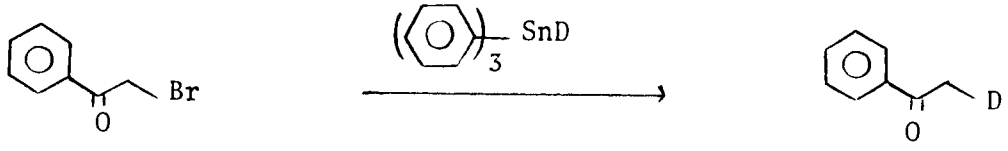
(1)

Catalytic hydrogenation in the presence of noble metals is a frequently employed method for achieving selective reductions. The compound to be reduced is placed in the presence of a catalyst and hydrogen; temperature, pressure, and solvent are varied to affect the desired reduction. The hydrogen and the functional groups to be reduced are adsorbed on the catalyst surface. The adsorption process distorts the bonds of the functional group to be reduced to the point that hydrogen will add across unsaturated carbon-carbon bonds. For example, the selective reduction of a double bond in the presence of a carbonyl is readily accomplished using palladium on charcoal (Eq. 2) [3].



(2)

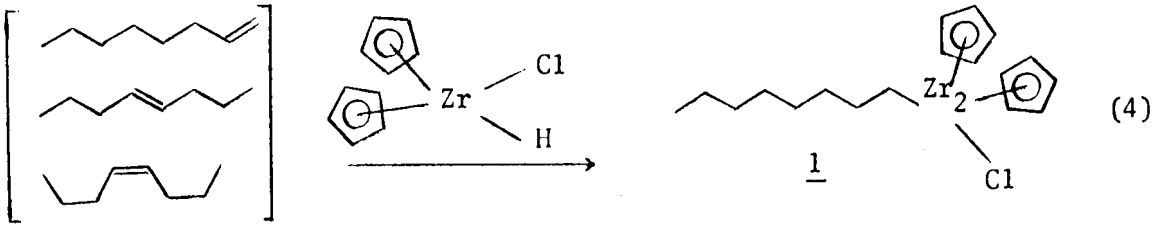
Triphenyltin hydride is a reducing agent that selectively reduces organic halides in the presence of other functional groups [4]. For example, the α-bromoketone is reduced to the α-deuterioketone using triphenyltin deuteride (Eq. 3) [5].



(3)

Recently, the reducing characteristics of DCCHZ [di(η^5-cyclopentadienyl)(chloro)hydrozirconium(IV)] were investigated [6,7]. DCCHZ reduces alkenes under mild conditions with rapid rearrangement to give the zirconium complex 1 in which Zr is attached to the least hindered

site (Eq. 4). The scope of the zirconium hydride reaction is not yet known. This is a new reagent that should be developed quickly because of its potential advantages over borane and alane [6].



1 (4)

Lithium aluminum hydride, sodium borohydride, and borane are of interest due to the fact that their reducing characteristics can be readily varied via replacement of a portion of the hydride units by other atoms or groups. Thus, $LiAlH_4$ (lithium aluminum hydride) reduces nearly all organic functional groups (Table I) [8,9]. However, substitution of three hydride units by t-butoxy groups forms lithium tri-t-butoxyaluminohydride which is a far more selective reducing agent (Table I) [10-13].

Sodium borohydride is a mild and selective reducing agent. It is used primarily for the reduction of aldehydes and ketones (Table I) [14]. It is interesting to note that substitution of hydride by methoxide produces a more reactive (less selective) reducing agent (Table I) [15].

Finally, borane complexes have been extensively investigated and their selectivity has been well documented by H. C. Brown and others [16]. Borane complexes are versatile reducing agents (Table I) [17-21].

TABLE I

SELECTIVITY EXHIBITED BY HYDRIDE REAGENTS

Functionality	$LiAlH_4$	$LiAlH(O\text{-}\underline{t}\text{-}Bu)_3$	$NaBH_4$	$NaBH(OMe)_3$	BH_3	$H\text{-}B(Sia)_2$[a]
Aldehyde	+[b]	+	+	+	+	+
Ketone	+	+	+	+	+	+
Acid chloride	+	+	+	+	-	-
Lactone	+	±	-	...	+	+
Epoxide	+	±	-	...	+	±
Ester	+	±	-	±	±	-
Carboxylic acid	+	-	-	+	+	-
Carboxylic acid salt	+	-	-	-	-	-
<u>tert</u>-Amide	+	-	-	...	+	+
Nitrile	+	-	-	±	+	-
Nitro	+	-	-	-	-	-
Olefin	-	-	-	-	+	+

[a] Sia = $-CH(CH_3)CH(CH_3)_2$.

[b] + indicates reaction readily occurs; ± indicates a slow reaction; - indicates little or no reaction occurs; ... indicates data not available.

Alkylboranes were also investigated by H. C. Brown. The reaction of borane with 2-methyl-2-butene gives disiamylborane which is a useful reducing agent (Table I) [17].

Dichloro- and monochloroborane are under investigation by H. C. Brown. However, there are few data available concerning the selectivity of mono- and dichloroborane [20,21]. Likewise, the reducing characteristics of alkoxyboranes—specifically dialkoxyboranes, 2—has not been investigated. The reducing characteristics of these interesting reagents will be discussed in subsequent chapters.

$(RO)_2B\text{-}H$

2

CHAPTER II

HISTORICAL BACKGROUND AND OBJECTIVE

Dialkoxyboranes are readily formed by the reaction of diborane with alcohols. The first dialkoxyborane (dimethoxyborane) was reported in 1933 and was prepared via the reaction of the corresponding alcohol and diborane (Eq. 5) [22].

$$4\ CH_3OH + B_2H_6 \longrightarrow 2(CH_3O)_2BH + 4H_2 \qquad (5)$$

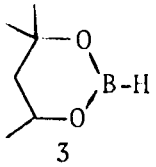
Glycols undergo an analogous reaction. Ethylene glycol and diborane react to give the dialkoxyborane, 1,3,2-dioxaborole (Eq. 6) [23].

$$2\ HOCH_2CH_2OH + B_2H_6 \longrightarrow 2 \left[\begin{array}{c} O \\ \diagup \\ \diagdown \\ O \end{array}\right] B\text{-}H + 4H_2 \qquad (6)$$

Both 1,3,2-dioxaborole and dimethoxyborane disproportionate readily at room temperature (Eq. 7). The problem of disproportionation

$$6\ (RO)_2BH \rightleftharpoons B_2H_6 + 4\ (RO)_3B \qquad (7)$$

was overcome by making 4,4,6-trimethyl-1,3,2-dioxaborinane, 3 [24].

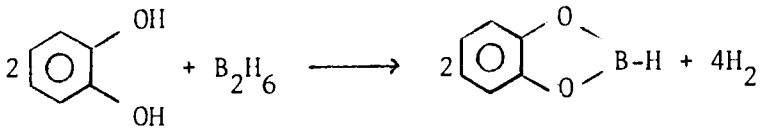


3

This reagent can be used for the hydroboration of alkenes [24] and

allenes [25], but it exhibits reduced reactivity relative to diborane, presumably due to π-bonding between boron and oxygen [24].

1,3,2-Benzodioxaborole, catecholborane, is a stable compound. Catecholborane, 4, is produced by the reaction of catechol and diborane (Eq. 8) [26]. It is a better hydroborating agent than the dialkoxyboranes [27]. The increased rate of hydroboration has been attributed to a decrease in π-bonding between oxygen and boron due to the

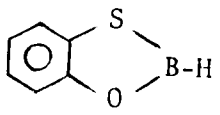


(8)

4

delocalization of the nonbonded p electrons over the aromatic ring.

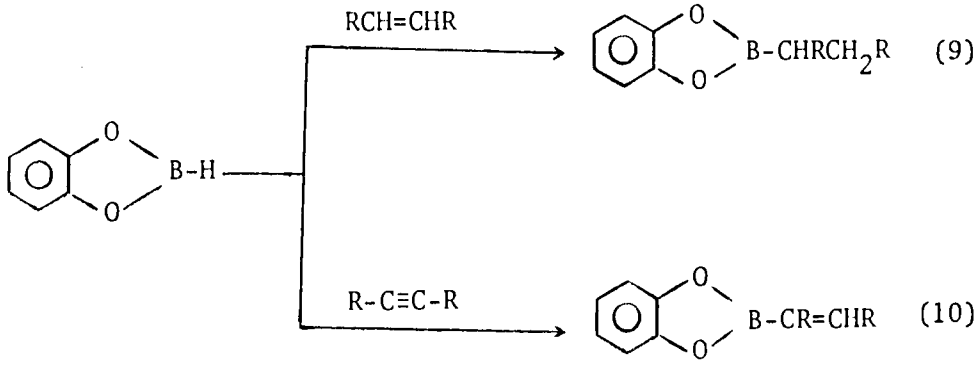
Of the various catechol derivatives imaginable, only one other compound has been investigated, 1,3,2-benzoxathiaborole, 5 [28]. There is little information currently available on this benzoxathiaborole, but investigation of its chemical properties or the dithio analog may provide interesting and valuable results.



5

The reduction of alkenes and alkynes by catecholborane has been extensively investigated [29-31]. Alkenes react with catecholborane to give the 2-alkyl-1,3,2-benzodioxaboroles in good yields (Eq. 9) [31].

Likewise, alkynes give 2-alkenyl-1,3,2-benzodioxaboroles in nearly quantitative yields (Eq. 10) [31].



Prior to this study, the reducing characteristics of CB had not been investigated [32]. Due to its reduced reactivity, it offered promise as a selective reducing agent.

Our objective was to explore the selective reducing properties of catecholborane toward a representative array of common functional groups, and to develop the unique chemistry of catecholborane.

CHAPTER III

REDUCTIONS UTILIZING CATECHOLBORANE

A. Conditions

Since this study was designed to determine the relative reactivity of catecholborane, CB, a standard set of conditions was selected. We chose to carry out the reactions at room temperature using stoichiometric amounts of hydride and substrate. The reactions were generally run in $CHCl_3$ with the initial concentration of the organic substrate at approximately 0.5 M. Increased reaction rates can be achieved by using excess hydride, raising the temperature, or increasing the concentration of the substrate.

It was found that the reaction rates were generally independent of the solvent utilized although the hydroboration of alkenes with CB exhibited a modest solvent dependence (Table II). Earlier studies revealed that the hydroboration of alkenes was solvent dependent [33].

B. Classification

The reactivity exhibited by the various functional groups toward CB in $CHCl_3$ can be classified for convenience into three broad categories:

(1) Fast—Those functional groups that react in approximately 24 hours or less (Table III).

(2) Slow—Those functional groups whose reaction times exceed 24 hours (Table IV).

TABLE II

REPRESENTATIVE EXAMPLES OF REDUCTIONS IN VARIOUS SOLVENTS[a]

Substrate	Solvent	Reduction Time (hr)	% Reduction[b]
$C_6H_{13}CH=CH_2$	$CHCl_3$	43.2	5
$C_6H_{13}CH=CH_2$	THF	46.5	25
Cyclohexene	$CHCl_3$	46	0[c]
Cyclohexene	THF	46	0[c]
Cyclopentanone	$CHCl_3$	72	68
Cyclopentanone	THF	72	71
Cyclohexanone	$CHCl_3$	24.6	84[c]
Cyclohexanone	Toluene	21	96[c]
$C_6H_{13}CHO$	$CHCl_3$	3	94
$C_6H_{13}CHO$	THF	3	87
$C_6H_{13}CHO$	Benzene	3.5	97

[a]Reductions were carried out using equimolar amounts of substrate and CB (concentration of reactants: $\sim$ 0.5 M) at room temperature.

[b]Reduction followed by GLC unless otherwise noted.

[c]Reduction followed by NMR.

TABLE III

FAST REACTING GROUPS[a]

Functional Group	Substrate	Ratio of H^-/Substrate	Time for 50% Reduction (min)	% Overall Reduction (time, hr)[b]	
ROH	$(CH_3)_3COH$	1:1	3	97[c]	(2.8)
	$(CH_3)_2CHOH$	1:1	4	95[c]	(2.9)
	CH_3CH_2OH	1:1	6	94[c]	(4.3)
	CH_3OH	1:1	13	87[c]	(6.0)
RCHO	$C_6H_{13}CHO$	1:1	3	89[d]	(3.0)
	$C_6H_{13}CHO$	1:1	3	93[e]	(3.0)
	$C_6H_{13}CHO$	1:1	3	97[f]	(3.0)
	$C_6H_{13}CHO$	1:1	9	86[g]	(3.0)
	C_6H_5CHO	1:1	35	85	(3.0)
	C_6H_5CHO	2:1	11	92	(1.5)
R_2CO	Cyclohexanone	1:1	75	86	(24)
	Cyclohexanone	1:1	18	95[h]	(21)
	Cyclohexanone	1:1	48	92[g,i]	(23.9)

TABLE III (continued)

Functional Group	Substrate	Ratio of H^-/Substrate	Time for 50% Reduction (min)	% Overall Reduction (time, hr)[b]
	2-Methyl-cyclohexanone	1:1	120	75 (15)
	4-t-Butyl-cyclohexanone	1:1	--	49[j] (4.5)
$R_2C=NR$	$C_6H_{13}C(CH_3)=NNHTs$	1:1	19	100 (0.92)
	$C_6H_{13}C(CH_3)=NN(CH_3)_2$	1:1	16	93 (0.83)
$R_2S=O$	$(CH_3)_2SO$	2:1	26	93 (24)
$R_3\overset{+}{N}\text{-}\overset{-}{O}$	$(CH_3)_3NO$	2:1	3	94 (8.5)
$(RCO)_2O$	$(C_3H_7CO)_2O$	4:1	68	79.5 (19.1)
Epoxide	Propylene Oxide	1:1	165	92[d,k] (26.5)
	Propylene Oxide	2:1	8	100[l] (1.0)
	Styrene Oxide	1:1	--	100[k] (0.25)

TABLE III (continued)

Functional Group	Substrate	Ratio of H^-/Substrate	Time for 50% Reduction (min)	% Overall Reduction (time, hr)[b]	
R-C≡C-H	$C_4H_9C{\equiv}CH$	1:1	738	78	(25)
	$C_4H_9C{\equiv}CH$	1:1	213	80[i]	(25)
	$C_4H_9C{\equiv}CH$	1:1	--	44[g,m]	(38)
	$C_4H_9C{\equiv}CH$	1:1	1388	51[g,i]	(25)
$RCH(OR)_2$	$C_6H_{13}CH(OC_2H_5)_2$	1:1	--	85.7	(19.2)
$R_2C(OR)_2$	1,1-Diethoxy-cyclohexane	1:1	--	94	(1.0)
RCOOH	$C_2H_5CO_2H$	3:1	1025	71	(24)

[a]Reactions were carried out using an initial substrate concentration of 0.5 M in $CHCl_3$ at room temperature unless specified otherwise. The times shown were obtained by interpolation of the data presented in the Appendix.

[b]Reduction followed by NMR unless specified otherwise.

[c]Reduction followed by monitoring the volume of H_2 gas evolved.

TABLE III (continued)

[d]Reduction followed by GLC.

[e]CB was rapidly injected into the reaction solution.

[f]This reaction was carried out using an initial substrate concentration of 0.5 M in benzene.

[g]This reaction was carried out using an initial substrate concentration of 0.5 M in THF.

[h]This reaction was carried out using an initial substrate concentration of 0.5 M in toluene.

[i]This reaction was carried out at reflux temperature.

[j]This ketone gave 85.4% axial and 14.5% equatorial products.

[k]The epoxide reacted with one equivalent of CB to give a mixture of products.

[l]Propylene oxide reacted with two equivalents of CB to give: $(CH_3)_2CHO(BC_6H_4O_2)$ (79%), $CH_3CH_2CH_2O(BC_6H_4O_2)$ (21%).

[m]This reduction was a slow reduction; to keep the alkyne reductions grouped together, this reduction was placed in the fast table.

TABLE IV

SLOW REACTING GROUPS[a]

Functional Group	Substrate	H^-/Substrate Ratio of	Time for 50% Reduction (hr)	% Overall Reduction (time, hr)[b]	
R_2CO	Cyclopentanone	1:1	28	70	(72)
	Cyclopentanone	1:1	28	70[c,d]	(72)
	$C_6H_{13}COCH_3$	1:1	40	70	(163)
	$C_6H_{13}COCH_3$	2:1	7.3	91	(71.8)
RCOCl	CH_3COCl	2:1	--	19[e]	(49.8)
R-C≡N	$C_2H_5C{\equiv}N$	2:1	48.6	54	(63)
$RCONR_2$	$CH_3CON(CH_3)_2$	2:1	--	40	(101)
	$CH_3CON(CH_3)_2$	3:1	9	70	(60.5)
	$CH_3CON(CH_3)_2$	3:1	--	100[f]	(20)
$RCH=CH_2$	$C_6H_{13}CH=CH_2$	1:1	--	5	(43.2)
	$C_6H_{13}CH=CH_2$	1:1	--	25[d]	(46.5)
	$C_6H_{13}CH=CH_2$	1:1	13.6	83[d,f]	(46.5)

TABLE IV (continued)

Functional Group	Substrate	Ratio of H^-/Substrate	Time for 50% Reduction (hr)	% Overall Reduction (time, hr)[b]	
RCO_2H	$PhCO_2H$	3:1	--	5	(24)

[a]Reactions were carried out using an initial substrate concentration of 0.5 M in $CHCl_3$ at room temperature unless specified otherwise. The times shown were obtained by interpolation of the data presented in the Appendix.

[b]Reduction followed by NMR unless specified otherwise.

[c]Reduction followed by GLC.

[d]This reaction was carried out using an initial substrate concentration of 0.5 M in THF.

[e]Initial substrate concentration was 1.66 M in $CHCl_3$.

[f]The reaction was carried out at reflux temperature.

(3) Inert—Those functional groups that exhibit no reactivity toward CB (Table V).

The data in the tables demonstrate that there was a wide range of reactivity within each category.

C. Acidic Proton Sources

As expected for an active metal hydride, CB readily reacted with active proton sources such as water, alcohols, and acids to liberate hydrogen (Eq. 11) over a one to two hour period.

$$ROH + CB \longrightarrow RO\text{-}B= + H_2 \qquad (11)$$

R=H; RCO-; Alkyl

D. Carbonyls and Derivatives

1. Aldehydes

The representative aliphatic and aromatic aldehydes were heptanal and benzaldehyde. Heptanal was rapidly and quantitatively reduced to the corresponding alkoxyborole, 6 (Eq. 12). Likewise, benzaldehyde was reduced rapidly to give the corresponding aryloxyborole. The borole derivatives were readily hydrolyzed to yield the corresponding

$$C_6H_{13}CHO + CB \longrightarrow RO\text{-}B= \xrightarrow{H_2O} C_6H_{13}CH_2OH \qquad (12)$$

6

alcohols upon addition of water.

TABLE V

GROUPS EXHIBITING NO REACTIVITY TOWARD CATECHOLBORANE[a]

Functional Group	Substrate	Ratio of H^-/Substrate	Reaction Time (hr)	% Reduction[b]
$R-CO_2R$	$C_3H_7CO_2C_2H_5$	1:1	81	0[c,d]
$R-S-S-R$	$(CH_3S)_2$	1:1	42.7	0
$R-NO_2$	CH_3NO_2	1:1	168	0
R_2SO_2	Tetramethylene sulfone	1:1	94	0
RCH=CHR	Cyclohexene	1:1	46	0
Lactone	Coumarin	1:1	96	0
$(RCO)_2O$	$(CF_3CO)_2O$	4:1	21	0[d]
	Succinic anhydride	4:1	50	0
R-Br	$\underline{n}-C_8H_{17}Br$	1:1	48	0
R-I	$\underline{n}-C_5H_{11}I$	1:1	48	0
R-COONa	$C_{17}H_{35}CO_2Na$	3:1	12	0[e]

[a]Reductions were carried out using an initial substrate concentration of 0.5 M in $CHCl_3$ at room temperature.

[b]Reduction followed by NMR unless otherwise noted.

[c]Reduction followed by GLC.

[d]These functional groups were partially reduced in two days when the reactions were carried out in THF.

[e]This salt was completely reduced in 6 hr when the reaction was carried out in THF.

2. Ketones

Cyclic and acyclic aliphatic ketones were reduced in high yields to give the corresponding alkoxyborole derivative, 7 (Eq. 13). 2-Octanone was chosen as a representative acyclic ketone; it was slowly reduced with one or two equivalents of hydride. On the other hand, cyclic ketones exhibited varying degrees of reactivity. For example,

$$R_2CO + CB \longrightarrow \underset{7}{R_2CHO\text{-}B=} \xrightarrow{H_2O} R_2CHOH \qquad (13)$$

cyclohexanone was reduced rapidly and was placed in the fast group. However, cyclopentanone reacted more slowly and was placed in the slow group (see Tables III and IV, pages 11 and 15). Differences in the reactivity of five and six member ring systems have been documented [34].

3. Hydrazone Derivatives

Two hydrazone derivatives were prepared and reduced. One was prepared using 2-octanone and p-toluenesulfonhydrazide to make the corresponding hydrazone, 8 (Eq. 14) via standard procedures [35]. The other was prepared using 2-octanone and unsymmetrical-N,N-

$$C_6H_{13}COCH_3 + NH_2NHTs \xrightarrow[\Delta,\ -H_2O]{EtOH} \underset{8}{C_6H_{13}C(NNHTs)CH_3} \qquad (14)$$

dimethylhydrazine to produce the corresponding N,N-dimethylhydrazone derivative, 9 (Eq. 15).

$$C_6H_{13}COCH_3 + NH_2N(CH_3)_2 \xrightarrow[\Delta,\ -H_2O]{EtOH} C_6H_{13}C(NN(CH_3)_2)CH_3 \quad (15)$$

9

These imine derivatives were among the most reactive species. These species reacted quantitatively with CB to give the corresponding hydrazine derivatives, 10 (Eq. 16).

$$C_6H_{13}C(NNR_2)CH_3 + CB \longrightarrow C_6H_{13}CH(N(B=)NR_2)CH_3 \quad (16)$$

$R=CH_3$, CH_3; H, Ts — 10

4. Acetals and Ketals

The reduction of acetals and ketals was examined since they are commonly utilized as protecting groups for ketones and aldehydes. CB was found to be reactive toward the ethyl ketal of cyclohexanone and the ethyl acetal of heptanal. Thus, it would appear that CB reductively cleaves acetals and ketals in a fashion analogous to borane complexes [36] to give the corresponding ether over a period of 24 hr (Eq. 17).

$$R_2C(OR)_2 \xrightarrow{H\text{-}B=} R_2CH(OR)$$

E. Acids, Acid Salts, Anhydrides, Acid Chlorides, Esters, and Amides

1. Acids

Aliphatic and aromatic acids reacted rapidly and quantitatively with one equivalent of CB to liberate hydrogen gas and form the corresponding acyloxyborane analogous to reductions involving borane

complexes [37,38], 11 (Eq. 18). The acyloxyborane, 11, reacted further with two additional equivalents of CB to give a

$$\underset{\text{R=aliphatic, aromatic}}{\text{RCOOH}} + \text{CB} \longrightarrow \underset{\underline{11}}{\text{RCOO-B=}} + H_2 \qquad (18)$$

quantitative yield of the corresponding alkoxyborane, 12 (Eq. 19) in the case of aliphatic acids. Attempts were made, by varying reaction

$$\text{RCOOB=} \xrightarrow{2\ \text{CB}} \underset{\underline{12}}{\text{RCH}_2\text{O-B=}} \xrightarrow{H_2O} \text{RCH}_2\text{OH} \qquad (19)$$

conditions, to produce the corresponding aldehyde from the acid precursor. However, only trace amounts of aldehyde were detected; presumably, reduction of the acyloxyborane, 11, is slow relative to reduction of the aldehyde formed during the reduction.

The aliphatic acid, propionic acid, reacted at a moderate rate. The aryl acid, benzoic acid, was found to react more slowly giving moderate yields of alcohol at reflux temperatures. Presumably, the reduced reactivity of benzoic acid is due to the weaker Lewis basicity of the carbonyl group in benzoic acid as compared to the carbonyl group in aliphatic acids.

2. Acid Salts

It was found that the sodium salt of stearic acid was not soluble in chloroform after the addition of CB and underwent no reduction. However, the sodium salt of stearic acid was rapidly reduced over a

period of 6.5 hr at room temperature in THF. This was a surprising result since borane complexes are reported to be inert toward the sodium salt of an acid [39].

3. Anhydrides

Anhydrides require four equivalents of CB. Presumably, the first equivalent of hydride produces the corresponding aldehyde and an acyloxyborole (Eq. 20). The proposed initial step prompted the investigation of the possibility of aldehyde production under varying

$$RCOOCOR + CB \longrightarrow RCHO + RCOO\text{-}B= \qquad (20)$$

reaction conditions. However, only trace amounts of aldehyde were detected in all cases. Presumably, the reduction of anhydride by CB was slow compared to the reduction of the aldehyde produced from the initial addition of CB to anhydride.

Butyric anhydride was rapidly reduced; after 20 hours, the reduction gave 86% of the 2-butroxy-1,3,2-benzodioxaborole, 13 (Eq. 21).

$$C_3H_7COOCOC_3H_7 \xrightarrow{CB} 2C_4H_9O(BC_6H_4O_2) \xrightarrow{H_2O} 2C_4H_9OH \qquad (21)$$

13

Trifluoroacetic anhydride and maleic anhydride were inert toward CB at room temperature in chloroform; however, trifluoroacetic anhydride reacted slowly when refluxed in $CDCl_3$.

4. Acid Chlorides

Acid chlorides, such as acetyl chloride, reacted very slowly taking two equivalents of CB to produce the corresponding alcohol. Presumably,

the reduction proceeded through initial reduction of the acid chloride to give the corresponding aldehyde which in turn was rapidly reduced to the corresponding alkoxyborole, 14 (Eq. 22). As expected, only a trace

$$RCOCl \xrightarrow{2\ CB} RCH_2O\text{-}B= \xrightarrow{H_2O} RCH_2OH \qquad (22)$$

14

of aldehyde was detected in this reduction. Overall, only low yields of the corresponding alcohol were realized.

5. Esters

Esters, such as ethyl butyrate, did not react at room temperature in $CHCl_3$ but did react slowly to give the corresponding alkoxyborole, 15 (Eq. 23), in fair to good yields when the reaction was carried out at reflux temperature in $CHCl_3$ or THF.

$$C_3H_7COOC_2H_5 \xrightarrow[2\ CB,\ \Delta]{THF\ or\ CHCl_3} C_3H_7CH_2O\text{-}B= \xrightarrow{H_2O} C_4H_9OH \qquad (23)$$

15

6. Amides

Primary and tertiary amides reacted with CB. The primary amide, acetamide, liberated 62% of the theoretical amount of hydrogen for the two amide hydrogens, and a mixture of products was produced. However, benzamide liberated two equivalents of hydrogen but did not undergo further reaction. The tertiary amide N,N-dimethylacetamide (DMAC) was reduced at room temperature to give the corresponding amine in 40% yield. It should be noted that DMAC was

cleanly reduced to the corresponding amine by utilizing a 50% excess of CB and running the reaction in refluxing chloroform solution for a period of 20 hr (Eq. 24).

$$CH_3CON(CH_3)_2 + 2\ CB \xrightarrow{\Delta,\ CHCl_3} CH_3CH_2N(CH_3)_2 \qquad (24)$$

F. Amine Oxide and Sulfoxide

Both the amine oxide and sulfoxide (Eqs. 25 and 26) reacted rapidly with two equivalents of CB to liberate one equivalent of hydrogen gas and to produce the deoxygenated amine and sulfide from the corresponding starting materials. By analogy with reductions using borane complexes [16] and from spectral data, the following reactions occurred (Eqs. 25 and 26). The liberation of hydrogen resulted from the reaction of CB with the acidic hydrogen of 16, produced as a common intermediate of the reductions.

$$(CH_3)_3NO + CB \longrightarrow (CH_3)_3N + \underset{\underline{16}}{H\text{-}O\text{-}B=} \qquad (25)$$

$$(CH_3)_2S{=}O + CB \longrightarrow (CH_3)_2S + \underset{\underline{16}}{H\text{-}O\text{-}B=} \qquad (26)$$

G. Alkenes and Alkynes

1. Alkenes

Terminal and internal alkenes were examined. CB reduced alkenes extremely slowly at room temperature with only 5% reduction of 1-octene over approximately a two-day period. This should allow many selective reductions of various functional groups in the presence of alkenes not possible for borane complexes. Good yields of the corresponding 2-alkyl-1,3,2-benzodioxaborole, 17 (Eq. 27), were obtained

$$RCH{=}CH_2 + CB \longrightarrow \underset{17}{RCH_2CH_2(BC_6H_4O_2)} \qquad (27)$$

when the reactions were carried out at 60-70° in THF. The rate of hydroboration of alkenes was somewhat solvent dependent (Table II, page 10). For example, 1-octene was hydroborated faster in a refluxing THF solution than in refluxing $CHCl_3$. This might be attributed to the catalytic action of ethers for the reduction of alkenes by boranes [33]. Under the given conditions, the hydroboration of 1-octene proceeded smoothly until it reached a maximum of approximately 81%; beyond this point, isomerization of 1-octene appeared to occur, producing increased amounts of internal alkene (presumably, via hydroboration-dehydroboration) with a concomitant decrease in yield of the alkylborane.

The secondary alkene cyclohexene was not hydroborated at room temperature in $CHCl_3$.

2. Alkynes

Terminal alkynes reacted much faster than alkenes. For example, hydroboration of 1-hexyne with CB was a fast reaction at room temperature producing the corresponding vinylborane in both THF and $CHCl_3$. Alkynes reacted with CB in a cis fashion [31] to yield 2-alkenyl-1,3,2-benzodioxaborole, 18 (Eq. 28) (a useful synthetic intermediate) [40,41]. Alkynes were selectively reduced in the presence of alkenes [42].

$$C_4H_9C{\equiv}CH + CB \longrightarrow C_4H_9CH{=}CH(BC_6H_4O_2) \quad (28)$$

18

H. Epoxides

Epoxides reacted with one equivalent of CB to give a mixture of products. Propylene oxide reacted rapidly and quantitatively with two equivalents of CB, ring opening to give the corresponding alcohols: 79% 2-propanol and 21% 1-propanol (Eq. 29).



$$\xrightarrow{2\ CB} \xrightarrow{H_2O} (CH_3)_2CHOH + CH_3CH_2CH_2OH \quad (29)$$

I. Nitro

Both the aliphatic nitro group of nitromethane and the aromatic nitro group of p-nitrophenylacetic acid were found to be inert at room temperature. The aromatic nitro group was unreactive even in refluxing $CHCl_3$ over a four-day period.

J. Nitrile

The nitrile group of propionitrile was found to react slowly at room temperature to give the corresponding amine borane, 19 (Eq. 30).

$$C_2H_5C{\equiv}N + 2\ CB \longrightarrow \underset{19}{C_3H_7N(B{=})_2} \qquad (30)$$

K. Sulfur Groups

As noted earlier, dimethylsulfoxide reacted rapidly with CB but tetramethylenesulfone and methyl disulfide were found to be inert toward CB at room temperature. The disulfide group was also found to be inert toward CB even in refluxing THF.

Methanesulfonic acid reacted with two equivalents of CB over a period of two to four hr to liberate the theoretical amount of hydrogen and to produce an unidentified product.

L. Lactone

The lactone, coumarin, was examined, and it was found to be inert toward CB at room temperature in $CHCl_3$.

M. Halides

Primary alkyl bromides and iodides were inert toward CB at room temperature, and primary alkyl bromides were also inert at reflux temperatures in chloroform over a period of two days.

CHAPTER IV

SELECTIVE REDUCTIONS UTILIZING CATECHOLBORANE

A systematic exploration of the reducing characteristics of CB revealed a broad range of reactivity toward various functional groups. This range of reactivity made possible many selective reductions.

Competitive experiments were performed; the substrates, in equal molar quantities, were allowed to compete for a limited quantity of CB. The more reactive functional groups were selectively reduced in the presence of less reactive groups.

The data in Table VI illustrate the selective reduction of an aldehyde in the presence of various functional groups. The data in Table VII demonstrate the selective reduction of a ketone in the presence of various functional groups. These data illustrate the utility of CB as a selective reducing agent.

Examination of Tables VI and VII reveals that CB is unique among the commonly used reducing agents. Thus, CB selectively reduced an aldehyde in the presence of a ketone (Table VI); this reduction is not possible using borane complexes. Also, in contrast to borane complexes, CB reacted with terminal alkynes to give the mono-hydroboration product, 20; furthermore, CB readily hydroborated alkynes in the presence of alkenes (Eq. 31).

$$C_4H_9C{\equiv}CH + \text{Cyclohexene} \xrightarrow{CB} C_4H_9CH{=}CHB{=} + \text{Cyclohexene} \quad (31)$$

20

TABLE VI

SELECTIVE REDUCTION OF HEPTANAL IN THE PRESENCE OF VARIOUS SUBSTRATES[a]

Substrate	% Unreacted Substrate[b]	% Heptanol[b,c]
$C_6H_{13}COCH_3$	93	94
$C_8H_{17}CH=CH_2$	97	99
Cyclohexene	100	100
$C_2H_5C\equiv N$	100	100
CH_3COCl	100	92[d]
$C_3H_7CO_2C_2H_5$	100	100
$\underline{n}$-$C_8H_{17}Br$	100	100

[a]Reductions were carried out using an initial substrate concentration of ∿0.5 M. CB was added dropwise to the solution maintained at -5°. The solution was stirred for 5 hr at -5°, warmed to 0° for 0.5 hr, stirred 6 hr at room temperature, quenched with water, and then analyzed.

[b]Reactions were analyzed by GLC unless specified otherwise.

[c]The product formed was the 2-heptoxy-1,3,2-benzodioxaborole.

[d]Reaction analyzed by NMR.

TABLE VII

SELECTIVE REDUCTION OF CYCLOHEXANONE IN THE PRESENCE OF VARIOUS SUBSTRATES[a]

Substrate	% Unreacted Substrate[b]	% Cyclohexanol[b,c]
$C_8H_{17}CH=CH_2$	100	98
Cyclohexene	100	98
$C_2H_5C\equiv N$	100	98
CH_3COCl	95	98[d]
$C_3H_7CO_2C_2H_5$	100	98
$\underline{n}$-C_4H_9Br	100	98

[a]Reductions were carried out using an initial substrate concentration of ∿0.5 M. CB was added to the solution maintained at -5°C. The solution was stirred for 5 hr at -5°, warmed to 0° and maintained for 0.5 hr, stirred 23 hr at room temperature, and then analyzed.

[b]Reactions were analyzed by GLC unless specified otherwise.

[c]The product formed was 2-cyclohexoxy-1,3,2-benzodioxaborole.

[d]Reaction analyzed by NMR.

CB did not cleave the disulfide linkage even at elevated temperatures; this is in contrast to sodium borohydride [43] and lithium aluminum hydride [44]. Thus, it appeared possible to reduce a variety of functional groups in the presence of the disulfide linkage; indeed, a number of acids were reduced in the presence of the disulfide group. Benzoic acid was reduced (100% formation of the borate ester) in the presence of methyl disulfide (Eq. 32). The acid functional group of D,L-thioctic acid was reduced (90% formation of the borate ester) in the presence of the disulfide functional group (Eq. 33) [45].

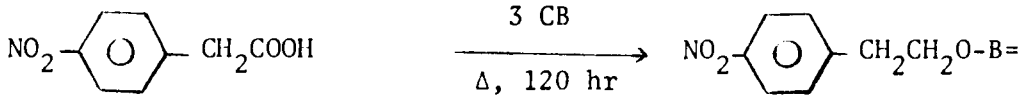
$$C_6H_5COOH + CH_3SSCH_3 \xrightarrow{120\ hr} C_6H_5CH_2O\text{-}B= + CH_3SSCH_3 \qquad (32)$$



(33)

Unlike lithium aluminum hydride [9], CB did not reduce alkyl halides or nitro compounds over long periods of time at room temperature; therefore, two functional groups were reduced in the presence of halides (Tables VI and VII) and many reductions should be possible in the presence of the nitro group since it did not react. For example, acids were quantitatively reduced in the presence of a bromide (Eq. 34) or a nitro group (Eq. 35).

$$CH_2BrCH_2COOH \xrightarrow[\Delta,\ 44\ hr]{6\ CB} CH_2BrCH_2CH_2O\text{-}B= \qquad (34)$$



(35)

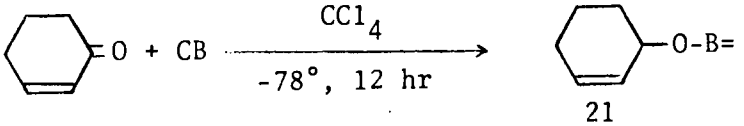
Esters were unreactive at room temperature. Thus, CB and borane complexes quantitatively reduced aldehydes (Table VI), ketones (Table VII), or acids in the presence of an ester (Eq. 36).

$$CH_3OCOCH_2CH_2COOH \xrightarrow[19.5\ hr]{4\ CB,\ R.T.} CH_3OCOCH_2CH_2CH_2O\text{-}B= \qquad (36)$$

Unlike borane complexes, CB reduced nitriles very slowly. Consequently, it was possible to reduce many of the functional groups present in Table III (page 11) in the presence of nitriles (Tables VI and VII) in quantitative yields (Eq. 37).

$$CH_3CH_2C{\equiv}N + C_6H_{13}CHO \xrightarrow{CB} CH_3CH_2C{\equiv}N + C_6H_{13}CH_2O\text{-}B= \qquad (37)$$

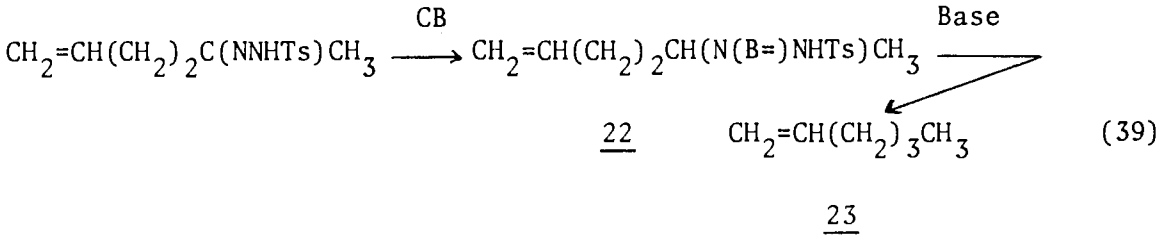
The CB reduction of enones resulted in good yields of enols. The quantitative reductions of an aldehyde and a ketone by CB in the presence of a terminal and disubstituted alkene were successfully achieved (Tables VI and VII). Thus, the reduction of the α,β-unsaturated ketone cyclohexenone gave good yields (87%) of the corresponding allylic compound, 21 (Eq. 38).



21 (38)

A hydrazone derivative was selectively reduced in the presence of a terminal alkene and a tosyl group to give the corresponding hydrazine derivative 22 in quantitative yield (Eq. 39). The reduction of a

hydrazone derivative by CB is analogus to the reduction of an oxime with a borane complex [46]. This valuable hydrazine intermediate was used for further transformations to give the corresponding hydrocarbon, 23 [47,48] via a new selective reduction procedure.



(39)

The deoxygenation of ketones and aldehydes will be explored more fully in the next chapter.

CHAPTER V

DEOXYGENATION PROCEDURES UTILIZING CATECHOLBORANE

A. Background

The classical reduction procedures for the conversion of carbonyls to methylene derivatives utilize strongly acidic conditions (Clemmensen) [49] or strongly basic conditions (Wolff-Kishner) [50] as well as high temperatures. These austere conditions preclude the presence of sensitive functional substituents. In addition, skeletal rearrangements are common for the strongly acidic conditions of the Clemmensen reduction. More recently, hydride reagents have been used for the conversion of the carbonyl carbon to a corresponding methyl or methylene carbon.

Complex metal hydrides, such as $LiAlH_4$ [51,52], $NaBH_4$ [51], $BH_3 \cdot THF$ [51], and $NaCNBH_3$ [35,53] have been used to reduce tosylhydrazone derivatives of aldehydes and ketones to the corresponding methyl and methylene derivatives. However, borane-methyl sulfide and substituted boranes had not been investigated as reducing agents for tosylhydrazone derivatives. We carried out preliminary investigations utilizing BMS (borane-methyl sulfide), 9-BBN (9-borabicyclo[3.3.1]nonane), and CB (catecholborane) to obtain background information. Eventually CB was chosen as the reducing agent because of the selectivity exhibited by CB toward tosylhydrazones.

The overall deoxygenation process for a ketone or aldehyde is as follows. A carbonyl compound is treated with p-toluenesulfonhydrazide

to give the corresponding tosylhydrazone derivative. The tosylhydrazone derivative is then treated with one of the hydride reagents to give an intermediate amine-borane complex similar to structure 22 (Eq. 39, p. 34). This complex is readily decomposed to give the deoxygenated methyl or methylene compound (Eq. 40).

$$RR'C{=}NNHTs \xrightarrow[2)\ Base]{1)\ H\text{-}B=} RR'CH_2 \qquad (40)$$

R′ = alkyl, aryl

R = H, alkyl

The results of our preliminary investigations utilizing borane-methyl sulfide and the substituted boranes are summarized below.

The tosylhydrazone of 2-octanone was reduced using a series of borane reagents. The reduction product was then decomposed in a variety of fashions. The data are presented in Tables VIII, IX and X for BMS, 9-BBN, and CB respectively.

Since the CB reductions gave excellent results, we briefly examined several different solvents in conjunction with $NaOAc \cdot 3H_2O$ in an attempt to optimize solvent conditions for the reaction. The results are summarized in Table XI.

B. Results and Discussion

1. Deoxygenation of Ketones

The CB procedure offers several unique advantages when compared to other metal hydrides: (1) CB is soluble in common organic solvents

TABLE VIII

REDUCTION OF THE TOSYLHYDRAZONE OF 2-OCTANONE UTILIZING BMS AND VARIOUS REAGENTS[a,b]

Reagent	Yield (%)[c]
HOAc	--[d]
H_2O	25
CH_3OH	46
NaOAc in HOAc	21
NaOAc in $HO(CH_2)_2OH$	32
$NaOCH_3$ in CH_3OH	69
$\underline{n}$-C_4H_9Li	29

[a]A 140% excess of hydride (BMS) was slowly added to a solution of the tosylhydrazone of 2-octanone in diglyme (0.4 M) at -5°. After the addition of BMS, the salt-ice bath was removed and the solution allowed to warm to room temperature. After 1.5 hr, 5 mL aliquots were removed from solution and quenched using various reagents at room temperature.

[b]NMR indicated that 92% of the hydrazone derivative was reduced by BMS after 1.5 hr.

[c]The yield of octane was determined by GLC.

[d]Only a trace of product was detected in this case.

TABLE IX

REDUCTION OF THE TOSYLHYDRAZONE OF 2-OCTANONE UTILIZING 9-BBN AND VARIOUS REAGENTS[a]

Reagent	Yield (%)[b]
HOAc	15
$BH_3 \cdot S(CH_3)_2$	7
H_2O	9
$NaOCH_3$ in CH_3OH	20

[a]9-BBN and the tosylhydrazone of 2-octanone were mixed in equal molar quantities at -5° in diglyme. To insure complete reduction of the hydrazone, the reaction was allowed to proceed for 9-10 hr. At the end of the 9-10 hr period, aliquots were quenched with the various reagents shown.

[b]The yield of octane was determined by GLC.

TABLE X

REDUCTION OF THE TOSYLHYDRAZONE OF 2-OCTANONE UTILIZING CB AND VARIOUS REAGENTS[a]

Reagent	Yield (%)[b]
$NaOCH_3$ in CH_3OH	59
NaI	--[c]
NaOAc in HOAc	66
$BF_3 \cdot O(C_2H_5)_2$	75
$SnCl_4$	--[d]
$NaOAc \cdot 3H_2O$	87

[a]CB and the tosylhydrazone of 2-octanone were mixed in equal molar quantities at 0° in CH_2Cl_2. The reaction was allowed to proceed for several minutes (45) at 0° and then various reagents were added to decompose the hydrazine complex.

[b]The yield of octane was determined by GLC.

[c]Only a trace of product was detected.

[d]After addition of $SnCl_4$, $NaOAc \cdot 3H_2O$ was added. There were approximately ten products produced by this reaction with only a trace of the desired product, octane.

TABLE XI

YIELD OF OCTANE IN VARIOUS SOLVENTS[a]

Solvent	Yield (%)[b]
$CHCl_3$	91
CH_2Cl_2	87
THF	78
Benzene	70
$(CH_3CH_2)_2O$	69

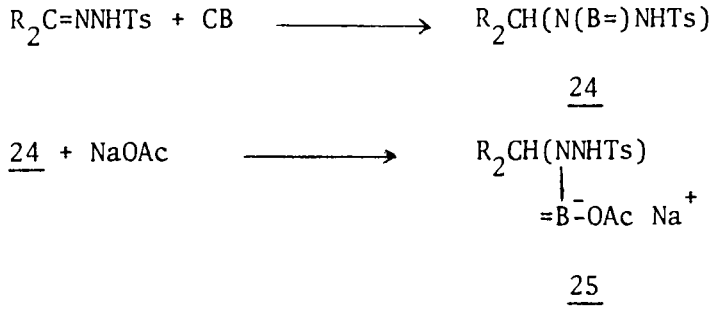
[a]CB and the tosylhydrazone of 2-octanone were mixed in approximately equal molar quantities at 0° (for benzene, the temperature was 6-10°) in the presence of $NaOAc \cdot 3H_2O$. The solutions were warmed slowly to room temperature. The reaction mixtures were allowed to stand for a minimum of 24 hr at room temperature.

[b]Yields were determined by GLC.

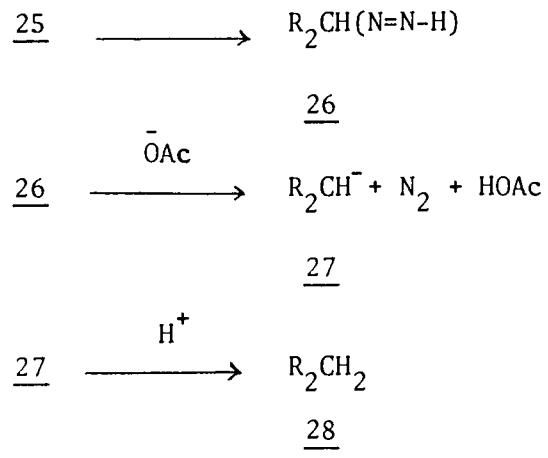
($CHCl_3$ or benzene) or it may be utilized neat; (2) CB will not affect many functional groups as demonstrated in Chapters III and IV; (3) a mild base ($NaOAC \cdot 3H_2O$) is used to obtain the final deoxygenated product; and (4) a low temperature (60°) is utilized for the decomposition step—alternatively, the same results were obtained by allowing the reaction mixture to sit for 24 hr at room temperature.

A reasonable mechanism is outlined in Scheme I. The tosylhydrazone derivative is reduced by CB to form the corresponding hydrazine complex, 24. Subsequently, the hydrazine complex, 25, is decomposed to give the diazene intermediate, 26. The elimination step that yields the diazene intermediate is analogous to other organoborane reactions; organoboranes which contain an electronegative substituent in the β position relative to the boron atom are prone to elimination, especially in the presence of nucleophiles [54-56]. The proposed diazene intermediate, 26, is unstable and decomposes to yield an alkane, 28, in the presence of a proton source [57]. Alternately, the diazene intermediate, 26, could decompose in a concerted fashion to give the product directly, 28.

Scheme I

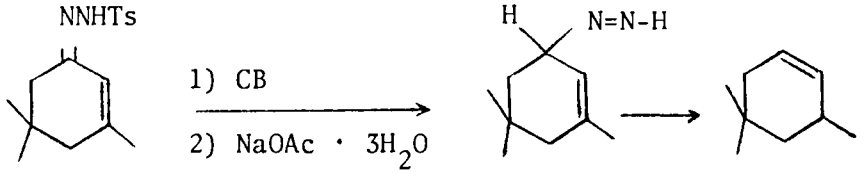


Scheme I, Continued



The reaction appears to be of general applicability, producing good yields of the corresponding reduction products. The reaction depends only on the availability and stability of the tosylhydrazone derivative used as starting material. Table XII summarizes the results of several reductions of ketones to the corresponding methylene derivatives.

For the α,β-unsaturated system (isophorone) in Table XII, the early results indicated that the reduction of the hydrazone derivative was accompanied by migration of the double bond (Eq. 41).



(41)

It was found that the migration of the double bond is a general phenomenon for α,β-unsaturated tosylhydrazone derivatives. The results are discussed in the next section.

TABLE XII

CONVERSION OF KETONES TO THE CORRESPONDING METHYLENE DERIVATIVES[a,b]

Ketone	Product	Yield (%)[c,d]
2-Octanone	Octane	91(81)[e]
Cyclohexanone	Cyclohexane	92
2-Methylcyclohexanone	Methylcyclohexane	77
2-Norboranone	Norbornane	63
Isophorone	3,5,5-Trimethylcyclohexene	41[f]

[a]The ketones were first converted to the corresponding tosylhydrazones.

[b]The tosylhydrazone to be reduced was dissolved in enough chloroform to give a 0.5 M solution. Then CB was added to the solution in a dropwise fashion at 0° and allowed to stand for 20-45 min. Sodium acetate trihydrate was then added and the reaction mixture was brought to a gentle reflux for 1 hr.

[c]Yields were determined by GLC analysis.

[d]GLC indicated no alkene formation.

[e]The number in parentheses indicates the isolated yield.

[f]In isophorone, the reduction and decomposition were accompanied by migration of the double bond.

2. Deoxygenation of α,β-Unsaturated Ketones and Aldehydes

The migration of the double bond in the α,β-unsaturated tosylhydrazone derivatives offers exciting synthetic possibilities such as the formation of the less stable positional isomers (exocyclic double bonds vs. endocyclic double bonds), deconjugation of conjugated double bonds, and exclusive formation of the trans isomer—when the possibility exists [53].

The reduction of α,β-unsaturated systems using the CB procedure to give the rearranged product offers a number of advantages when compared to similar reactions: (1) the reaction requires only one equivalent of hydride but can tolerate a large excess; (2) it is carried out under mild conditions (61°, $NaOAc \cdot 3H_2O$); (3) common aprotic organic solvents are utilized, such as chloroform; (4) clean isomerizations are obtained with no alkane formation; (5) the trans isomer is formed exclusively; and (6) deuterium is incorporated in a regiospecific manner. The results of the reduction of several α,β-unsaturated ketone and aldehyde tosylhydrazone derivatives are summarized in Table XIII.

The results obtained for the reduction of α,β-unsaturated systems support a concerted decomposition of the diazene intermediate: (1) the least stable alkene is formed exclusively in a number of instances; (2) the double bond always migrated from the original position in a predictable fashion; (3) the trans isomer is formed exclusively when the possibility exists; (4) there is 100% deuterium incorporation in a regiospecific manner for the isophorone derivative to give 3,5,5-trimethylcyclohexene-3-d, 29; and (5) the tosylhydrazone of cholest-4-en-3-one gives 5-β-cholest-3-ene (cis ring juncture).

TABLE XIII

DEOXYGENATION OF α,β-UNSATURATED CARBONYL COMPOUNDS UTILIZING CB[a,b]

Carbonyl	Product	Yield (%)
trans-1-Phenyl-1-buten-3-one	trans-1-Phenyl-2-butene	73[c] (48)[d]
trans-Cinnamaldehyde	3-Phenyl-1-propene	53[c]
Mesityl oxide	trans-4-Methyl-2-pentene	65[c]
1-Acetylcyclohexene	Ethylidenecyclohexane	77[c] (68)[d]
Isophorone	3,5,5-Trimethylcyclohexene	66[e]
Isophorone	3,5,5-Trimethylcyclohexene-3-d	66[e,f]
Cholest-4-en-3-one	5-β-Cholest-3-ene	98[e] (89)[g]

[a]The carbonyl compounds were first converted to the corresponding tosylhydrazones.

[b]Generally, the tosylhydrazones were dissolved in chloroform (0.5 M) at 0°. CB was added (5-10% excess) and the reduction allowed to proceed for 2 hr at 0°. Sodium acetate trihydrate was added and the reaction mixture was brought to a gentle reflux for 1 hr.

[c]Yield was determined by GLC.

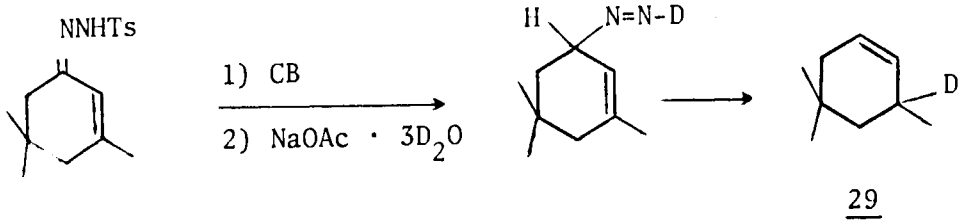
[d]The numbers in parentheses refer to the isolated yields. Products were obtained by filtering the reaction mixture through silica gel.

[e]Yield was determined by NMR.

[f]$NaOAc \cdot 3D_2O$ was utilized in place of $NaOAc \cdot 3H_2O$.

[g]This number is an isolated yield obtained by chromatographing the product over alumina.

Control experiments clearly demonstrated that the deuterium-hydrogen exchange occurs rapidly in the tosylhydrazones. Consequently, it is likely that deuterium is incorporated at some stage prior to the diazene decomposition as demonstrated in the case of isophorone (Eq. 42).



(42)

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CHAPTER VI

EXPERIMENTAL

A. Analytical Equipment and Commercial Reagents

A Varian Aerograph model 1700 and an Aerograph model A-700 gas chromatograph, equipped with either a Leeds and Northrup Speedomax or a Varian recorder, were used for analysis and yield determinations. The flow rate for the carrier gas was 60 ml/min for both instruments.

The analytical columns used in the Varian Aerograph were a 10-ft, 10% silver nitrate on polypropylene glycol and a 6-ft, 5% SE-30 on Chromosorb W. The analytical column used in the Aerograph was a 10-ft, 10% SE-30 on Chromosorb W.

The NMR spectra were obtained with a Varian T-60 and A-60 spectrometer, using carbon tetrachloride, chloroform, chloroform-d, toluene, benzene, and THF as solvents, and TMS (tetramethylsilane) as an internal standard. The chemical shifts were recorded in δ units, ppm downfield from TMS.

The IR spectra were obtained using a Beckman IR5A spectrophotometer, calibrated with a polystyrene film. The absorptions were reported in microns.

Optical rotation was measured for solutions in chloroform using a Josef and Jan Fric Model 2477 spectropolarimeter.

Except as noted, the reagents, which were obtained commercially for these investigations, were used without further purification. The respective chemicals and their sources are shown in Table XIV.

TABLE XIV

SOURCE OF COMMERCIAL REAGENTS

Reagent	Source
Acetamide	E[a]
Acetic Acid	F[b]
Acetic Anhydride	F
Acetyl Chloride	E
1-Acetylcyclohexene	A[c]
Anisole	E
Benzaldehyde	E
Benzene	F
Benzoic Acid	A
Borane-Methyl Sulfide	A
Boron Trifluoride·Etherate	E
1-Bromobutane	E
1-Bromooctane	E
tert-Butyl Alcohol	F
4-tert-Butylcyclohexanone	A
Catechol	A
Carbon Tetrachloride	F
Chloroform	F
Chloroform-d	M
trans-Cinnamaldehyde	E
Coumarin	A
Cyclohexanone	F
Cyclohexene	E
Cyclopentanone	B[d]
1,5-Cyclooctadiene	A
Decane	E
1-Decene	A
Deuterium Oxide	BR[e]
N,N-Dimethylacetamide	E
n-Dodecane	A
Ethanol	F
Ethyl Butyrate	E
Ethyl Ether	F
Heptanal	M[f]
Heptane	E
Hexanoic Acid	E
5-Hexene-2-one	A
1-Hexyne	FR[g]
1-Iodopentane	E
Isophorone	A
Ligroin	F
Lithium Aluminum Hydride	V[h]
Maleic Anhydride	A

TABLE XIV (continued)

Reagent	Source
Mesityl Oxide	E
Methanol	F
Methanesulfonic Acid	E
2-Methoxyethyl Ether	A
2-Methylcyclohexanone	A
Methyl Disulfide	A
Methylene Chloride	F
mono-Methyl Succinate	A
Methyl Sulfoxide	F
Nitromethane	F
n-Nonane	A
2-Norbornanone	A
n-Octane	A
2-Octanone	E
1-Octene	A
Pentane	E
trans-1-Phenyl-1-buten-3-one	E
Phenylethylene Oxide	E
2-Propanol	F
Propionitrile	E
Propylene Oxide	E
Sodium Acetate	F
Sodium Acetate·Trihydrate	F
Sodium Borohydride	V
Sodium Stearate	F
n-Tetradecane	A
Tetrahydrofuran	F
Tetramethylene Sulfone	A
Toluene	F
p-Toluenesulfonhydrazide	A
n-Tridecane	A
Triethyl Orthoformate	E
Trifluoroacetic Anhydride	A
Trimethylamine-N-Oxide	E
n-Undecane	A

[a]E = Eastman Kodak Company.

[b]F = Fisher Scientific Company.

[c]A = Aldrich Chemical Company.

[d]B = J. T. Baker Chemical Company.

[e]BR = Bio·Rad Laboratories.

TABLE XIV (continued)

[f]M = Matheson, Coleman and Bell.

[g]FR = Farchan Research Laboratories.

[h]V = Ventron Corporation.

B. Preparation of Reagents

1. Dry THF

THF (1.25 L) was added to a 2-L flask fitted with a drying tube and magnetic stirring bar. Approximately 5-10 g of $LiAlH_4$ was added slowly to the stirred solution of THF. After stirring overnight, the THF was distilled, bp 65°, under a nitrogen atmosphere in flame-dried glassware and collected in a 1-L flask fitted with a septum. After completion of the distillation, the THF was stored under nitrogen at 0°. The $LiAlH_4$ was destroyed cautiously with ethyl acetate and water. CAUTION: Do not distill the THF to dryness!

2. Dry Diglyme

Diglyme (1.2 L) was added to a 2-L flask followed by the slow addition of 6 g of $LiAlH_4$. After sitting overnight, the diglyme was distilled, bp 34° at 0.2 mm, and collected in a 1-L flask equipped with a septum inlet. After completion of the distillation, the diglyme was stored under nitrogen at 0°.

3. Borane·THF [58]

A 2-L, 3-necked flask was equipped with a magnetic stirring bar, a 250-mL pressure equalizing dropping funnel fitted with a stopple (for subsequent addition of BF_3·etherate) and a Dry Ice-acetone condenser. The condenser was connected to a three-way stopcock which was connected to a mercury bubbler (which acts as a safety pressure release) and to two gas traps in series. The gas traps were connected to a fritted, gas-dispersion tube. The assembled apparatus was then flame-dried and flushed with nitrogen. The fritted glass tube was immersed in a 1-L flask

containing THF (800 mL), a magnetic stirring bar, and fitted with a septum inlet. A second mercury bubbler was connected to the septum inlet for gas pressure release. Sodium borohydride (73 g) and dry diglyme (750 mL) were placed in the reaction flask. The dropping funnel was charged with boron trifluoride etherate (313 mL of a 42% solution). Sodium borohydride (4 g) was placed in the first Dry Ice-acetone trap along with dry diglyme (30 mL). The 1-L receiving flask and the gas traps were cooled to 0° and -78°, respectively. The Dry Ice-acetone condenser on the reaction flask was also charged.

The boron trifluoride etherate was added to the reaction flask over a 5-hr period at room temperature. After addition of the boron trifluoride etherate, the reaction mixture was heated for 1 hr at 60°. The BH_3·THF solution was stored under nitrogen at 0°. The solution was standardized by measuring the amount of hydrogen evolved by the hydrolysis of an aliquot using a water:glycerine (50:50) solution. The BH_3·THF solution was 2.14 M in borane.

4. Catecholborane [59]

BH_3·THF, 396 mL (0.77 mol) of a 2.14 M solution, was placed in a flame-dried, nitrogen-purged reaction flask equipped with a dropping funnel, mercury bubbler, and stirring bar. The dropping funnel was charged with 77.2 g (0.70 mol) of catechol (dried over calcium chloride) dissolved in 200 mL of dry THF. The BH_3·THF solution was added dropwise at 0° over a 6-hr period with stirring. After the addition of catechol was complete, the reaction mixture was allowed to warm slowly to room temperature and was stirred overnight to complete

the reaction. The THF was removed at room temperature under reduced pressure using a standard distillation set-up with a Vigreaux column (27 cm). The reduced pressure was achieved using a water aspirator connected to the distillation apparatus via a $CaCl_2$ drying tube. After removing most of the THF, the remaining solution was fractionally distilled under reduced pressure yielding 39.5 g (47%) of catechol-borane, bp 40° at 26 mm (lit. bp 76° at 99 mm).

5. 9-BBN (9-Borabicyclo[3.3.1]nonane) [60]

Borane·THF (44.3 mL, 0.10 mol) was added to a flame-dried, nitrogen-purged 100-mL round-bottom flask equipped with a septum inlet, a dropping funnel, a mercury bubbler, and a mechanical stirrer. The dropping funnel was charged with cyclooctadiene (12.2 mL, 0.10 mol) dissolved in anhydrous THF (50 mL). The solution of borane·THF was cooled to -5° using a salt-ice bath. The cyclooctadiene solution was added to the stirred solution of borane·THF over a 30- to 60-min period. The reaction solution was heated to reflux for 1 hr. The solution was allowed to stir overnight at room temperature. It was cooled to -78° using a Dry Ice-acetone bath. The 9-BBN crystallized from the THF solution. The liquid was removed using a syringe. The solid was filtered in a dry box under a nitrogen atmosphere and was washed with 2 x 50-mL of pentane at 0°. The white crystalline solid was stored under nitrogen atmosphere at 0°.

6. Ethanol Free Chloroform

Chloroform (2 L) was washed with three 30-mL portions of concentrated sulfuric acid followed by four 100-mL water washes to remove the

commercial stabilizer ethanol. The solution was dried over magnesium sulfate and distilled, bp 62°, from fresh magnesium sulfate. The chloroform was stored in the dark at 0° under a nitrogen atmosphere.

7. 1,1-Diethoxycyclohexane

Cyclohexanone (31.1 mL, 0.3 mol), triethyl orthoformate (60 mL, 0.36 mol), 100 mL of THF, and a catalytic amount of p-toluenesulfonic acid were placed in a round-bottom flask equipped with distillation head, condenser, and a receiving flask. The flask was heated so that a slow rate of distillation was achieved. The distillation was carried out over a three-hour period removing most of the THF. The remaining material was washed with 2 x 50-mL portions of water containing 0.5 mL of acetic acid; subsequently, 2 x 50-mL-washes of saturated sodium carbonate were applied. The organic layer was separated, dried over anhydrous magnesium sulfate, and distilled, bp 60-62° at 6.2 mm (lit. bp 61-62° at 7 mm) [61]. NMR (neat, external TMS): 3.43 (4H, q, J = 7.0 Hz, $-OCH_2CH_3$), 1.53 (10H, m, $-CH_2-$), 1.13 (6H, t, J = 7.0 Hz, $-CH_3$).

8. 1,1-Diethoxyheptane

Heptanal (50 mL, 0.372 mol), triethyl orthoformate (74 mL, 0.443 mol), 100 mL of THF, and a catalytic amount of p-toluenesulfonic acid were placed in a round-bottom flask equipped with a distillation head, condenser, and a receiving flask. The flask was heated and the solvent slowly distilled. The distillation was carried out over a three-hour period removing most of the THF. The remaining material was washed with two 50-mL portions of water containing 0.5 mL of acetic acid followed by two washes (50 mL) of saturated sodium carbonate. The organic layer was

separated, dried over magnesium sulfate, and distilled, bp 67.5-69° at 3.2 mm (lit. bp 54-57° at 9 mm) [62]. NMR (neat, external TMS): 4.87 (t, 1H, $-\underline{CH}(OCH_2CH_3)_2$), 3.87 (m, 4H, $-O-\underline{CH_2}CH_3$), 1.44 (m, 19H, $-CH_2-$ and $-CH_3$).

9. Anhydrous Trimethylamine-N-Oxide

Commercial trimethylamine-N-oxide dihydrate was sublimed at 0.5 mm and 80°. NMR confirmed there was no water present. NMR ($CHCl_3$): 3.13 (s, $(CH_3)_3N-O$).

10. unsym-N,N-Dimethylhydrazine of 2-Octanone

unsymmetrical-N,N-Dimethylhydrazine (3.82 mL, 0.05 mol), 2-octanone (7.82 mL, 0.050 mol), absolute ethanol (10 mL), and a catalytic amount of fuming sulfuric acid were mixed and refluxed for 1-1.5 hr. The solvent was removed and the unsym-N,N-dimethylhydrazone of 2-octanone was distilled, bp 192° at atmospheric pressure. NMR (neat, external TMS): 0.67 (m, 3H, $\underline{CH_3}CH_2-$), 1.07 (m, 8H, $-\underline{CH_2}-$), 1.60 (s, 3H, $\underline{CH_3}-C=N-$), 1.87 (m, 2H, $-\underline{CH_2}C=N-$), 2.07 (s, 6H, $-N(\underline{CH_3})_2$).

11. Tosylhydrazones (General)

Tosylhydrazones of various ketones were prepared via a standard procedure [35]. The p-toluenesulfonhydrazide (5-10% excess) was heated with a given ketone in absolute ethanol at reflux temperature (30-60 min) without acid or base catalysis. The solution was then cooled to 0-5° and the corresponding tosylhydrazones were crystallized, filtered, and dried in vacuo at room temperature.

C. CB Reductions

Unless stated otherwise, reductions were performed in dry, nitrogen-flushed reaction flasks. The flask (25 mL) was charged with 2.5 mmol of starting material and 5.0 mL of $CHCl_3$. Subsequently, CB (2.63 mmol, 5% excess) was added dropwise to the stirred solution at room temperature over a 2- to 3-min period. Reactions were followed by GLC, NMR, or gas evolution. The times used to compose the tables of Chapter III were obtained by interpolation of the data in the Appendix, Tables XV to XXXIX.

1. 2-Methyl-2-propanol in $CHCl_3$ (XV)

The reaction of 2-methyl-2-propanol (0.470 mL, 5.00 mmol) in $CHCl_3$ (10 mL) with CB (0.565 mL, 5.25 mmol) was followed by monitoring gas evolution using a gas buret.

2. 2-Propanol in $CHCl_3$ (XVI)

The reaction of 2-propanol (0.383 mL, 5.00 mmol) in $CHCl_3$ (10 mL) with CB (0.565 mL, 5.25 mmol) was followed by monitoring the gas evolution using a gas buret. An NMR spectrum of the resultant borate ester ($(CH_3)_2CH$-O-B=) indicated a down-field shift of the methyl and methyne protons. NMR ($CHCl_3$, TMS): 4.68 (1H, heptet, J = 6 Hz, $(CH_3)_2\underline{CH}$-O-B=), 1.33 (6H, d, J = 6 Hz, $(CH_3)_2CH$-O-B=).

3. Ethanol in $CHCl_3$ (XVII)

The reaction of ethanol (0.584 mL, 5.00 mmol) in $CHCl_3$ (10 mL) with CB (0.55 mL, 5.25 mmol) was followed by monitoring the gas evolution using a gas buret. An NMR spectrum of the resultant borate ester

(CH_3CH_2-O-B=) indicated a down-field shift of the methyl and methylene protons. NMR ($CHCl_3$): 4.18 (q, J = 7 Hz, $CH_3\underline{CH_2}$-O-B=), 1.34 (t, J = 7 Hz, $\underline{CH_3}CH_2$-O-B=).

4. Methanol in $CHCl_3$ (XVIII)

The reaction of methanol (0.202 mL, 5.00 mmol) in $CHCl_3$ (10 mL) with CB (0.565 mL, 5.25 mmol) was followed by monitoring the gas evolution using a gas buret. An NMR spectrum of the resultant borate ester (CH_3-O-B=) indicated a down-field shift of the methyl protons. NMR ($CHCl_3$): 3.83 (s, $\underline{CH_3}$-O-B=).

5. Heptanal (XIX)

a. In $CHCl_3$. The reduction of heptanal (0.36 mL, 2.50 mmol) in $CHCl_3$ (5.0 mL) by CB (0.253 mL, 2.63 mmol) was followed by using NMR to monitor the formation of the resultant borate ester compared to the methyl and methylene protons (-$(\underline{CH_2})_4\underline{CH_3}$). NMR ($CHCl_3$): 4.67 (t, $CH_3(CH_2)_5\underline{CH_2}$-O-B=), 1.30 (m, -$(CH_2)$-$_5$), 0.83 (m, $\underline{CH_3}$-).

b. In $CHCl_3$. The reduction of heptanal (0.670 mL, 5.00 mmol) in $CHCl_3$ (10 mL) by rapid injection of CB (0.571 mL, 5.25 mmol) was followed by GLC. The internal standard, n-undecane (0.240 mL, 1.14 mmol), was added. The reduction was followed by monitoring the disappearance of the starting material.

c. In Benzene. The reduction of heptanal (0.350 mL, 2.61 mmol) in benzene (5.0 mL) by CB (0.284 mL, 2.61 mmol) was followed by GLC. An internal standard, n-undecane (0.120 mL, 0.569 mmol), was added and, at various intervals, aliquots of the solution were withdrawn and quenched with water. The reaction mixtures were analyzed by monitoring the disappearance of the starting material.

d. In THF. The reduction of heptanal (0.335 mL, 2.5 mmol) in THF (5.0 mL) by CB (0.272 mL, 2.50 mmol) was followed by GLC. An internal standard, n-undecane (0.120 mL, 0.569 mmol), was added and, at various intervals of time, aliquots of the solution were withdrawn and quenched with water. The reaction was followed by monitoring the disappearance of the starting material.

6. Benzaldehyde (XX)

a. In $CHCl_3$. The reduction of benzaldehyde (0.255 mL, 2.5 mmol) in $CHCl_3$ (5.0 mL) by CB (0.283 mL, 2.63 mmol) was followed by NMR. An internal standard, toluene (0.177 mL, 1.67 mmol), was added. The reduction was followed by monitoring the formation of the resultant borate ester. NMR ($CHCl_3$): 5.17 (s, $PhC\underline{H}_2$-O-B=).

b. In $CHCl_3$. The reduction of benzaldehyde (0.254 mL, 2.5 mmol) by CB (0.548 mL, 5.25 mmol) was followed by NMR in $CHCl_3$ (10 mL) containing a small amount of ethanol as preservative. An internal standard, toluene (0.177 mL, 1.67 mmol), was added. The reduction was followed by monitoring the formation of the resultant borate ester. NMR ($CHCl_3$): 5.23 (s, $PhC\underline{H}_2$-O-B=).

7. Cyclohexanone (XXI)

a. In $CHCl_3$. The reduction of cyclohexanone (0.259 mL, 2.5 mmol) by CB (0.283 mL, 2.63 mmol) was followed by NMR. An internal standard, CH_2Cl_2 (0.250 mL, 3.90 mmol), was added. The reduction was followed by monitoring the formation of the resultant borate ester. NMR ($CHCl_3$): 4.33 (m, $C_4H_8C\underline{H}$-O-B=).

b. Toluene. The reduction of cyclohexanone (0.259 mL, 2.5 mmol) in toluene (5.0 mL) by CB (0.287 mL, 2.63 mmol) was followed by NMR. An internal standard, 1,2-dichloroethane (0.050 mL, 0.625 mmol), was added. The reduction was followed by monitoring the formation of the resultant borate ester. NMR (toluene): 4.33 (m, $C_4H_8\underline{CH}$-O-B=).

c. In Refluxing THF. The reduction of cyclohexanone (0.259 mL, 2.5 mmol) in refluxing THF (5.0 mL) by CB (0.290 mL, 2.63 mmol) was followed by GLC. The internal standard, n-undecane (0.240 mL, 1.14 mmol), was added and, at various intervals of time, aliquots of the solution were withdrawn and quenched with water. The reaction was then followed by monitoring the disappearance of the starting material using GLC.

8. 2-Methylcyclohexanone in $CHCl_3$ (XXII)

The reduction of 2-methylcyclohexanone (0.307 mL, 2.5 mmol) in $CHCl_3$ (5.0 mL) by CB (0.283 mL, 2.63 mmol) was followed by NMR. The reaction was followed by monitoring the formation of the resultant borate ester compared to the ring and methyl hydrogens. NMR ($CHCl_3$): 4.67 (m, $C_6H_{12}\underline{CH}$-O-B=), 4.23 (m, $C_6H_{12}\underline{CH}$-O-B=). Presumably the two peaks are due to cis and trans isomers.

9. 4-t-Butylcyclohexanone in $CHCl_3$ (XXIII)

The reduction of 4-t-butylcyclohexanone (0.411 g, 2.66 mmol) in $CHCl_3$ (5.0 mL) by CB (0.305 mL, 2.79 mmol) was followed by NMR. The reaction was followed by monitoring the formation of the resultant borate ester compared to the ring and t-butyl hydrogens. NMR analysis revealed that 85.4% of the oxygen in the borate ester was in

the axial conformation. NMR ($CHCl_3$): 4.67 (m, equatorial borate ester, $C_9H_{18}\underline{C}H$-O-B=), 4.13 (m, axial borate ester derivative, $C_9H_{18}\underline{C}H$-O-B=).

10. Tosylhydrazone of 2-Octanone in $CHCl_3$ (XXIV)

The reduction of the tosylhydrazone of 2-octanone (0.740 g, 2.5 mmol) in $CHCl_3$ (5.0 mL) (a trace of ethanol is present as a preservative) by CB (0.271 mL, 2.73 mmol) was followed by NMR. The reaction was followed by monitoring the disappearance of the methyl group attached to the imine carbon (relative to the benzylic methyl group). NMR ($CHCl_3$): 2.37 (s, $-SO_2C_6H_4\underline{C}H_3$), 2.20 (s, $\underline{C}H_3(C_6H_{13})C$=N-).

11. Unsymmetrical-Dimethylhydrazone of 2-Octanone in $CHCl_3$ (XXV)

The reduction of the dimethylhydrazone of 2-octanone (0.452 g, 2.5 mmol) in $CHCl_3$ (5.0 mL) by CB (0.271 mL, 2.63 mmol) was followed by NMR. The reduction was followed by monitoring the disappearance of the methyl group attached to the imine carbon (relative to the N-methyl groups). NMR ($CHCl_3$): 2.47 (s, $-N(\underline{C}H_3)_2$), 1.93 (s, $\underline{C}H_3(C_6H_{13})C$=N-).

12. Sodium Stearate in THF

Sodium stearate (0.306 g, 1.00 mmol), dried in a desiccator using P_4O_{10} as a desiccant, was mixed with CB (0.328 mL, 3.0 mmol) in THF (10 mL). After quenching the reaction with water, the water was removed and the product was dissolved in pyridine. The reaction was complete in 6.5 hr. NMR analysis indicated a 100% yield of the corresponding octadecanol. NMR (Pyridine): 3.37 (m, 2H, $-CH_2\underline{C}H_2$-O-), 0.90 (m, 35H, $C_{17}H_{35}$).

13. Dimethylsulfoxide in $CHCl_3$ (XXVI)

The reduction of $(CH_3)_2S$=O (0.177 mL, 2.5 mmol) in $CHCl_3$ (5.0 mL) by CB (0.542 mL, 5.26 mmol) was followed by NMR. An internal standard,

anisole (0.300 mL, 2.76 mmol), was added. The reaction was followed by monitoring the appearance of the dimethyl sulfide product. NMR ($CHCl_3$): 2.10 (s, $(CH_3)_2S$).

14. Trimethylamine-N-Oxide in $CHCl_3$ (XXVII)

The reduction of $(CH_3)_3N$-O (0.188 g, 2.5 mmol) in $CHCl_3$ (5.0 mL) by CB (0.542 mL, 5.26 mmol) was followed by NMR. An internal standard, anisole (0.300 mL, 2.76 mmol), was added. The reduction rate was followed by monitoring the appearance of trimethylamine. NMR ($CHCl_3$): 2.63 (s, $(CH_3)_3N$).

15. n-Butyric Anhydride in $CHCl_3$ (XXVIII)

The reduction of $(C_3H_7CO)_2O$ (0.409 mL, 2.5 mmol) in $CHCl_3$ (5.0 mL, containing ethanol as a preservative) by CB (1.16 mL, 10.7 mmol) was followed by NMR. The reduction was followed by monitoring the disappearance of the methylene hydrogens adjacent to the acyl carbon (compared to the hydrogens on the α carbon in the borate ester ($-CH_2O-B=$)). NMR ($CHCl_3$): 4.13 (t, $C_3H_7\underline{CH}_2$-O-B=).

16. Propylene Oxide (XXIX)

a. In $CHCl_3$. The reaction of propylene oxide (0.169 mL, 2.5 mmol) in $CHCl_3$ (5.0 mL, containing ethanol as a preservative) by CB (0.276 mL, 2.5 mmol) was followed by GLC. An internal standard, n-undecane (0.150 mL, 0.71 mmol), was added. The CB was added to the reaction mixture at 0° and the solution was allowed to warm to room temperature. The reaction was followed by monitoring the rate of disappearance of starting material. The NMR spectrum indicated a complicated mixture.

b. In $CHCl_3$. The reduction of propylene oxide (0.169 mL, 2.5 mmol) in $CHCl_3$ (5 mL) by CB (0.573 mL, 5.25 mmol) was followed by NMR. An internal standard, CH_2Cl_2 (0.200 mL, 3.12 mmol), was added. The reaction was followed by monitoring the appearance of either the primary borate ester derivative or the secondary borate ester derivative. NMR ($CHCl_3$): 4.67 (septet, J = 6 Hz, $(CH_3)_2\underline{CH}$-O-B=), 1.37 (d, J = 6 Hz, $(\underline{CH_3})_2$CH-O-B=); 4.07 (t, $CH_3CH_2\underline{CH_2}$-O-B=), 0.93 (t, $\underline{CH_3}CH_2CH_2$-O-B=).

17. Styrene Oxide in $CHCl_3$

The reduction of styrene oxide (0.287 mL, 2.5 mmol) in $CHCl_3$ (5.0 mL) by CB (0.277 mL, 2.63 mmol) was monitored by NMR. After 15 min, the NMR spectrum indicated all the starting material had disappeared and a complicated reaction mixture resulted. The complicated spectrum was probably the result of polymerization of the styrene oxide. The reaction was not investigated further.

18. 1-Hexyne (XXX)

a. In $CHCl_3$. The reduction of 1-hexyne (0.287 mL, 2.5 mmol) in $CHCl_3$ (5.0 mL) by CB (0.287 mL, 2.63 mmol) was followed by NMR. An internal standard, phenanthrene (0.225 g, 1.26 mmol), was added. The reaction was followed by monitoring the appearance of the vinylic hydrogen on the carbon attached to the boron compared with the internal standard, phenanthrene. The terminal vinylic hydrogen to the boron is a doublet with triplet fine structure. The coupling constant of 18 Hz is characteristic of trans coupling across a double bond resulting from cis addition to the terminal alkyne to give the trans product [24]. NMR ($CHCl_3$): 5.75 (d, J = 18 Hz, C_4H_9CH=$\underline{CH}$B=).

b. In Refluxing $CHCl_3$. The reduction of 1-hexyne (0.287 mL, 2.5 mmol) in refluxing $CHCl_3$ (5.0 mL) by CB (0.287 mL, 263 mmol) was followed by NMR. An internal standard, 1,2-dichloroethane (0.200 mL, 2.5 mmol), was added. The reaction was followed by monitoring the appearance of the terminal vinylic hydrogen of the borane derivative compared with the internal standard. NMR ($CHCl_3$): 5.72 (d, J = 18 Hz, $C_4H_9CH=C\underline{H}B=$).

c. In THF. The reduction of 1-hexyne (0.287 mL, 2.5 mmol) in THF (5.0 mL) by CB (0.285 mL, 2.63 mmol) was followed by NMR. An internal standard, phenanthrene (0.223 g, 1.23 mmol), was added. The reduction was followed by monitoring the appearance of the terminal vinylic hydrogen of the borane derivative compared with the internal standard. NMR (THF): 5.62 (d, $C_4H_9CH=C\underline{H}B=$).

d. In Refluxing THF. The reduction of 1-hexyne (0.287 mL, 2.5 mmol) in refluxing THF (5.0 mL) by CB (0.285 mL, 2.63 mmol) was followed by NMR. An internal standard, benzene (0.741 mL, 0.833 mmol), was added. The reduction was followed by monitoring the appearance of the terminal vinylic hydrogen of the borane derivative compared with the internal standard. NMR (THF): 5.72 (d, $C_4H_9CH=C\underline{H}B=$).

19. 1,1-Diethoxyheptane in $CHCl_3$

The reduction of 1,1-diethoxyheptane (0.469 g, 2.50 mmol) in $CHCl_3$ (5.0 mL) by CB (0.285 mL, 2.63 mmol) was followed by NMR. An internal standard, CH_2Cl_2 (0.200 mL, 3.12 mmol), was added. The reduction was followed by monitoring the disappearance of the methyne proton

on the acetyl carbon. The NMR spectrum indicated an 85.7% reduction after 19.2 hr based on the formation of ethoxyborole derivative. NMR ($CHCl_3$): 4.07 (q, $CH_3\underline{CH}_2$-O-B=).

20. 1,1-Diethoxycyclohexane in $CHCl_3$

The reduction of 1,1-diethoxycyclohexane (0.430 g, 2.5 mmol) in $CHCl_3$ (5.0 mL) by CB (0.255 mL, 2.63 mmol) was followed by NMR. An internal standard, CH_2Cl_2 (0.200 mL, 3.12 mmol), was added. The reduction was followed by monitoring the formation of the ether and borate ester derivative. NMR indicated a 94% yield after 1 hr. NMR ($CHCl_3$): 4.13 (q, $CH_3\underline{CH}_2$-O-B=), 3.40 (q, $C_5H_{10}CHO\underline{CH}_2CH_3$), 3.30 (m, $C_5H_{10}\underline{CH}O$-).

21. Propionic Acid in $CHCl_3$ (XXXI)

The reduction of propionic acid (0.187 mL, 2.5 mmol) in $CHCl_3$ (5.0 mL) containing the commercial stabilizer ethanol by CB (0.855 mL, 7.88 mmol) was followed by NMR. The reaction was followed by monitoring the formation of the borate ester compared to the methylene hydrogens α to the acyl carbon. NMR ($CHCl_3$): 4.14 (t, $CH_3CH_2\underline{CH}_2$-O-B=).

22. Cyclopentanone (XXXII)

a. In $CHCl_3$. The reduction of cyclopentanone (0.222 mL, 2.5 mmol) in $CHCl_3$ (5.0 mL) by CB (0.283 mL, 2.63 mmol) was followed by NMR. The reduction was followed by monitoring the formation of the borate ester. NMR ($CHCl_3$): 4.90 (m, $C_4H_8\underline{CH}$-O-B=), 1.70 (m, $C_4\underline{H}_8CH$-O-B=).

b. In THF. The reduction of cyclopentanone (0.222 mL, 2.5 mmol) in $CHCl_3$ (5.0 mL) by CB (0.286 mL, 2.63 mmol) was followed by GLC. An internal standard, n-dodecane (0.105 mL, 0.462 mmol), was added. Aliquots

were withdrawn at various time intervals and quenched with water. The reaction was followed by monitoring the disappearance of the starting material compared to the internal standard.

23. 2-Octanone (XXXIII)

a. In $CHCl_3$. The reduction of 2-octanone (0.391 mL, 2.5 mmol) in $CHCl_3$ (5.0 mL) by CB (0.283 mL, 2.63 mmol) was followed by NMR. An internal standard, CH_2Cl_2 (0.250 mL, 3.90 mmol), was added. The reduction was followed by monitoring the formation of the borate ester relative to the internal standard or with the hydrogens present in the starting material. NMR ($CHCl_3$): 4.50 (m, $(CH_3)(C_6H_{13})\underline{CH}$-O-B=).

b. In $CHCl_3$. The reduction of 2-octanone (0.391 mL, 2.5 mmol) in $CHCl_3$ (5.0 mL) by CB (0.565 mL, 5.25 mmol) was followed by NMR. An internal standard, CH_2Cl_2 (0.250 mL, 3.90 mmol), was added. The reduction was followed by monitoring the formation of the borate ester compared with the internal standard or with the hydrogens present in the starting material. NMR ($CHCl_3$): 4.50 (m, $(CH_3)(C_6H_{13})\underline{CH}$-O-B=).

24. Acetyl Chloride in $CHCl_3$ (XXXIV)

The reduction of acetyl chloride (0.350 mL, 5.0 mmol) in $CHCl_3$ (3.0 mL) by CB (1.13 mL, 10.5 mmol) was followed by NMR. The methyl group of acetyl chloride was the internal standard. The reduction was followed by monitoring the formation of the borate ester compared to the methyl group attached to the acyl carbon of the starting material. NMR ($CHCl_3$): 4.13 (q, $CH_3\underline{CH_2}$-O-B=), 1.27 (t, $\underline{CH_3}CH_2$-O-B=).

25. Propionitrile in $CHCl_3$ (XXXV)

The reduction of propionitrile (0.357 mL, 5.0 mmol) in $CHCl_3$ (10 mL) by CB (1.15 mL, 10.5 mmol) was followed by NMR. An internal standard anisole (0.361 mL, 3.32 mmol) was added. The reduction was followed by monitoring the formation of the boron-amine derivative compared with the internal standard. NMR ($CHCl_3$): 3.47 (t, $CH_3CH_2\underline{CH}_2$-N-$(B=)_2$), 1.6 (q of doublets, $CH_3\underline{CH}_2CH_2$-N-$(B=)_2$), 0.90 (t, $\underline{CH}_3CH_2CH_2$-N-$(B=)_2$).

26. N,N-Dimethylacetamide (XXXVI)

a. In $CHCl_3$. The reduction of N,N-dimethylacetamide (0.232 mL, 2.5 mmol) in $CHCl_3$ (5.0 mL) by CB (0.565 mL, 5.25 mmol) was followed by NMR. The reduction was followed by monitoring the protons present in the starting material relative to those of the tertiary amine product dimethylethylamine. NMR ($CHCl_3$): 1.17 (t, $\underline{CH}_3CH_2N(CH_3)_2$).

b. In $CHCl_3$. The reduction of N,N-dimethylacetamide (0.232 mL, 2.5 mmol) in $CHCl_3$ (5.0 mL) by CB (0.696 mL, 7.88 mmol) was followed by NMR. The reduction was followed by monitoring the protons present in the starting material relative to those of the tertiary amine product, dimethylethylamine. NMR ($CHCl_3$): 1.17 (t, $\underline{CH}_3CH_2N(CH_3)_2$).

c. N,N-Dimethylacetamide in $CHCl_3$. The reduction of N,N-dimethylacetamide (0.232 mL, 2.5 mmol) in refluxing $CHCl_3$ (5.0 mL) containing a commercial stabilizer ethanol by CB (0.855 mL, 7.88 mmol) was followed by NMR. The NMR spectrum indicated a 100% yield after 20 hr. NMR ($CHCl_3$): 3.17 (q, 2H, $CH_3\underline{CH}_2N(CH_3)_2$), 2.57 (s, 6H, $CH_3CH_2N(\underline{CH}_3)_3$), 1.30 (t, 3H, $\underline{CH}_3CH_2N(CH_3)_2$).

27. 1-Octene (XXXVII)

a. In $CHCl_3$. The reduction of 1-octene (0.392 mL, 2.5 mmol) in $CHCl_3$ (5.0 mL) containing the commercial stabilizer ethanol by CB (0.276 mL, 2.5 mmol) was followed by GLC. The internal standard, n-nonane (0.60 mL, 3.36 mmol), was added. Aliquots were withdrawn periodically and quenched with water. The reduction was followed by monitoring the disappearance of the starting material relative to the internal standard.

b. In THF. The reduction of 1-octene (0.392 mL, 2.5 mmol) in THF (5.0 mL) by CB (0.301 mL, 2.63 mmol) was followed by GLC. The internal standard, n-nonane (0.600 mL, 3.36 mmol), was added. Aliquots were withdrawn periodically and quenched with water. The reduction was followed by monitoring the disappearance of the starting material compared to the internal standard.

c. In Refluxing THF. The reduction of 1-octene (0.392 mL, 2.5 mmol) in refluxing THF (5.0 mL) by CB (0.301 mL, 2.63 mmol) was followed by GLC. The internal standard, n-nonane (0.600 mL, 3.36 mmol), was added. Aliquots were withdrawn periodically and quenched with water. The reduction was followed by monitoring the disappearance of the starting material compared to the internal standard. During the course of the reduction, a shoulder appeared on the starting material peak that was first noticed after 17.5 hrs. The shoulder was assumed to be isomerized alkene (2-octene) produced by hydroboration-dehydroboration to give the internal alkene. After four days, there appeared to be 39% of the alkene remaining with the majority of this being the assumed 2-octene.

28. Ethyl Butyrate (XXXVIII)

a. In Refluxing $CHCl_3$. The reduction of ethyl butyrate (0.330 mL, 2.5 mmol) in refluxing $CHCl_3$ (5.0 mL, with the commercial stabilizer ethanol present) by CB (0.581 mL, 5.25 mmol) was followed by GLC. An internal standard, n-nonane (0.400 mL, 2.24 mmol), was added. The reduction was followed by monitoring the disappearance of the starting material compared to the internal standard after quenching aliquots with water.

b. In Refluxing THF. The reduction of ethyl butyrate (0.330 mL, 2.5 mmol) in refluxing THF (5.0 mL) by CB (0.581 mL, 5.25 mmol) was followed by GLC. An internal standard, n-nonane (0.400 mL, 2.24 mmol), was added. The reduction was followed by monitoring the disappearance of the starting material compared to the internal standard after quenching aliquots with water.

29. Trifluoroacetic Anhydride in Refluxing $CDCl_3$ (XXXIX)

The reduction of trifluoroacetic anhydride (0.065 mL, 0.462 mmol) in refluxing $CDCl_3$ (1.0 mL) by CB (0.214 mL, 1.94 mmol) was followed by NMR. An internal standard, toluene (0.0328 mL, 0.308 mmol), was added. The reduction was followed by monitoring the appearance of the borate ester. NMR ($CDCl_3$): 4.40 (q, 8 Hz, CF_3CH_2-O-B=).

30. Benzoic Acid in $CHCl_3$

The reduction of benzoic acid (0.305 g, 2.50 mmol) in $CHCl_3$ (5.0 mL) by CB (0.840 mL, 7.88 mmol) was followed by NMR. An internal standard, anisole (0.177 mL, 1.67 mmol), was added. NMR indicated a 5% reduction to form the corresponding borate ester after 24 hr. NMR ($CHCl_3$): 5.17 (s, $PhCH_2$-O-B=).

D. Attempted Reductions Summarized in Chapter III (Table V, page 18)

The following entries in Table V were shown to undergo no reduction: ethyl butyrate, methyl disulfide, nitromethane, sulfolane, cyclohexene, coumarin, trifluoroacetic anhydride, 1-iodopentane, and sodium stearate. The compounds were all found to undergo no reduction when 2.5 mmol of a given compound was dissolved in 5 mL of $CHCl_3$ at room temperature and allowed to react for the times shown and for the equivalents of CB used for each case listed in Table V. It should be noted, however, that various functionalities were reduced under modified conditions. Ethyl acetate was reduced by CB at reflux temperatures in the THF and in $CHCl_3$. The sodium salt of an acid was reduced by CB in THF but not in $CHCl_3$.

E. CB Selective Reductions

1. Heptanal (Table VI, page 29)

a. Heptanal with Cyclohexene, Propionitrile, Ethyl Propionate, and 1-Bromooctane. Heptanal (0.336 mL, 2.5 mmol) was reduced in the presence of cyclohexene (0.253 mL, 2.5 mmol), propionitrile (0.176 mL, 2.5 mmol), ethyl propionate (0.332 mL, 2.5 mmol), and 1-bromooctane (0.434 mL, 2.5 mmol) in $CHCl_3$ (4.0 mL) by CB (0.283 mL, 2.5 mmol). An internal standard, n-decane (0.195 mL, 1.0 mmol), was added. The CB was added at -5° and the solution was allowed to slowly warm to room temperature over a 1-hr period. The solution was allowed to sit at room temperature for approximately 12 hr and then examined by GLC. GLC indicated that the aldehyde

was quantitatively reduced with no reduction of cyclohexene, propionitrile, ethyl propionate, and 1-bromooctane (see Table VI, page 29). The NMR spectrum showed the absence of the aldehydic proton of heptanal.

b. Heptanal with 1-Decene. Heptanal (0.336 mL, 2.5 mmol) was reduced in the presence of 1-decene (0.473 mL, 2.5 mmol) in $CHCl_3$ (5.0 mL) by CB (0.288 mL, 2.63 mmol). An internal standard, n-undecane (0.322 mL, 1.52 mmol), was added. The CB was added at 0° and the solution was allowed to slowly warm to room temperature over a 1 hr period. The solution was allowed to sit at room temperature for 17 hr and analyzed by GLC. GLC indicated 99% of the heptanal was reduced with 3% reduction of 1-decene.

c. Heptanal with Acetyl Chloride. Heptanal (0.336 mL, 2.5 mmol) was reduced in the presence of acetyl chloride (0.178 mL, 2.5 mmol) in $CHCl_3$ (5.0 mL) by CB (0.283 mL, 2.63 mmol). Two internal standards were necessary: n-undecane (0.300 mL, 1.42 mmol) for GLC analysis of heptanal and CH_2Cl_2 (0.080 mL, 1.25 mmol) for NMR analysis of acetyl chloride. CB was added and the solution was maintained at 0° for 0.5 hr. The solution was then allowed to warm to room temperature. After sitting 8 hr at room temperature, the solution was examined by GLC and NMR. GLC indicated 92% of the heptanal was reduced. The NMR spectrum indicated 0% reduction of acetyl chloride.

d. Heptanal with 2-Octanone. Heptanal (0.336 mL, 2.5 mmol) was reduced in the presence of 2-octanone (0.391 mL, 2.5 mmol) in $CHCl_3$ (5.0 mL) by CB (0.283 mL, 2.63 mmol). An internal standard, n-undecane

(0.500 mL, 2.37 mmol), was added. CB was added and the solution was maintained at -5° for 0.5 hr. The solution was warmed and the temperature maintained at 0° for 0.5 hr. The solution was then allowed to warm to room temperature. The solution was maintained at room temperature approximately 4 hr before being analyzed by GLC. GLC indicated 94% of the heptanal was reduced with 7% reduction of 2-octanone.

2. Cyclohexanone (Table VII, page 30)

a. Cyclohexanone with 1-Bromobutane, Cyclohexene, 1-Decene, Propionitrile, and Ethyl Propionate. Cyclohexanone (0.259 mL, 2.5 mmol) was reduced in the presence of 1-bromobutane (0.269 mL, 2.5 mmol), cyclohexene (0.253 mL, 2.5 mmol), 1-decene (0.473 mL, 2.5 mmol), propionitrile (0.176 mL, 2.5 mmol), and ethyl propionate (0.332 mL, 2.5 mmol) in $CHCl_3$ (2.71 mL) by CB (0.283 mL, 2.63 mmol). An internal standard, n-undecane (0.528 mL, 2.5 mmol), was added. CB was added at -5° followed by the removal of the salt-ice bath. The solution was allowed to slowly warm to room temperature (1 hr). The solution was stirred at room temperature for approximately 5 hr before being analyzed by GLC. GLC indicated a 98% reduction of cyclohexanone with 0% reduction of 1-decene, 1-bromobutane, cyclohexene, propionitrile, and ethyl propionate.

b. Cyclohexanone with Acetyl Chloride. Cyclohexanone (0.259 mL, 2.5 mmol) was reduced in the presence of acetyl chloride (0.178 mL, 2.5 mmol) in $CHCl_3$ (5.0 mL) by CB (0.283 mL, 2.63 mmol). Two internal standards were necessary: n-undecane (0.300 mL, 1.42 mmol) for GLC analysis of cyclohexanone and CH_2Cl_2 (0.080 mL, 1.25 mmol) for NMR

analysis of acetyl chloride. CB was added at 0° followed by removal of the ice bath thus allowing the solution to warm to room temperature (1 hr). The solution sat at room temperature for approximately 4 hr before being analyzed by NMR and GLC. GLC indicated 98% reduction of cyclohexanone with 5% reduction of acetyl chloride.

3. CB Reduction of 1-Hexyne in the Presence of Cyclohexene

1-Hexyne (0.0574 mL, 0.5 mmol) was reduced in the presence of cyclohexene (0.0411 mL, 0.5 mmol) in $CDCl_3$ (1.0 mL) by CB (0.058 mL, 0.535 mmol). The internal standard, 1,2-dichloroethane (0.0197 mL, 0.25 mmol), was added and the reaction was followed by NMR. CB was added at 0° and the solution was allowed to warm slowly to room temperature. After the solution stirred for 7 days at room temperature, 82.3% of the 1-hexyne had reacted and 99.3% of the cyclohexene remained. NMR ($CDCl_3$): 5.53 (d, C_4H_9CH=CHB=, partially obscured by the vinyl protons of the cyclohexene); 5.66 (s, -CH=CH- of cyclohexene).

4. CB Reduction of Benzoic Acid in the Presence of Methyl Disulfide

Benzoic acid (0.056 g, 0.462 mmol) was reduced in the presence of methyl disulfide (0.0435 g, 0.462 mmol) in $CDCl_3$ (1.0 mL) by CB (0.20 mL, 1.85 mmol). Methyl disulfide was used as the internal standard and reactant. The reaction was followed by NMR. CB was added at 0° and the solution allowed to warm slowly to room temperature. The NMR tube was then heated on a steam bath. After 120 hr, 99.8% of the benzoic acid had reacted and 100% of the methyl disulfide remained. NMR ($CDCl_3$): 5.03 (s, $PhC\underline{H}_2$-O-B=); 2.30 (s, $(C\underline{H}_3$-S-$)_2$).

5. CB Reduction of DL-Thioctic Acid

DL-Thioctic acid (0.0477 g, 0.231 mmol) was reduced in $CDCl_3$ (1.0 mL) by CB (0.0805 mL, 0.742 mmol). CB was added at room temperature and the solution was allowed to sit 43 hr at room temperature. The solution was then heated on a steam bath for 66 hr. NMR indicated a 90% yield of the corresponding borate ester without polymerization of the disulfide linkage. Addition of water gave the corresponding alcohol. The alcohol was identified by comparing the NMR of the alcohol with the starting material DL-thioctic acid (Sadtler No. 10147). NMR ($CDCl_3$): 4.9 (s, -OH), 3.63 (m, 3H, -CHRS and $-CH_2O-$), 3.13 (t, 2H, $-CH_2S-$), 2.4 (sextet, 2H, ring $-SCH_2\underline{CH_2}-$), 1.53 (m, 8H, $-(CH_2)-_4$).

6. CB Reduction of 3-Bromopropionic Acid

3-Bromopropionic acid (0.071 g, 0.462 mmol) was reduced in $CDCl_3$ (1.0 mL) by CB (0.30 mL, 2.77 mmol). CB was added at room temperature and the solution was allowed to sit for 28 hr at room temperature. The solution was then heated on a steam bath for 16 hr giving 100% of the corresponding borate ester by NMR. Water was added to free the alcohol from the borate ester. The solvent was evaporated and the product chromatographed on silica gel using petroleum ether and 2% ethyl ether by volume. The first component was 3-bromopropanol (bp 75-77° at 14 mm, lit. 75.5-77° at 14 mm) [63]. NMR ($CDCl_3$): 2.1 (pentet, 2H, $-\underline{CH_2}-$), 3.5 (t, 2H, $-\underline{CH_2}Br$), 3.9 (t, 2H, $-\underline{CH_2}O-$), 4.2 (s, 1H, $-\underline{OH}$).

7. CB Reduction of 4-Nitrophenylacetic Acid

4-Nitrophenylacetic acid (0.0543 g, 0.963 mmol) was reduced in $CDCl_3$ (2.3 mL) by CB (0.104 mL, 0.963 mmol). CB was added at 0° and

the solution was subsequently heated on a steam bath for 266.2 hr giving 89.5% of the borate ester by NMR without detectible reduction of the nitro group. Water was added and the solution extracted with ether. The ether was washed with 1.0 N sodium hydroxide. The solvent was evaporated and the solid was chromatographed on silica gel using ether. The solid obtained was recrystallized from methanol and water (mp 64°, lit. 64°) [64]. NMR ($CDCl_3$): 3.0 (t, 2H, $-CH_2Ar$), 3.9 (t, 2H, $-CH_2O$), 5.2 (s, 1H, -OH), 7.33 and 8.10 (A_2X_2, 4H, Ar).

8. CB Reduction of mono-Methyl Succinate

mono-Methyl succinate (0.365 g, 2.77 mmol) was reduced in $CHCl_3$ (5.53 mL) by CB (1.25 mL, 11.61 mmol). CB was added at room temperature and the solution was allowed to react for 19.5 hr giving 94.7% of the borate ester by NMR from the acid without detectible reduction of the methyl ester. Water was added and the solution extracted with ether. The ether was evaporated and the organic material chromatographed over silica gel using petroleum ether and ether (65% by volume). Fractions two and three were collected and distilled to give γ-butyrolactone (bp 205° at 750 mm, lit. 206° at 760 mm) [65]. NMR ($CDCl_3$): 4.4 (t, 2H, $-CH_2O-$), 2.5 (complex m, 4H, $-CH_2CH_2CO-$).

9. CB Reduction of 2-Cyclohexen-1-one

The reduction of 2-cyclohexen-1-one in CCl_4 or $CHCl_3$ at room temperature with one equivalent of CB gave a complicated mixture. However, the reduction of 2-cyclohexen-1-one (0.250 mL, 5.25 mmol) in CCl_4 (5 mL) with CB (0.570 mL, 1.08 mmol) was monitored using benzene (0.074 mL, 0.832 mmol) as an internal standard giving 87% of the allylic borate

ester by NMR after 12 hr. The product was identified by comparing the product NMR with Sadtler No. 21066. NMR (CCl_4): 5.83 (m, -CH=CH-), 4.83 (m, C_5H_8CH-O-B=), 1.97 (broad m, $-(CH_2)-_3$).

10. CB Reduction of the Tosylhydrazone of 5-Hexen-2-one

The tosylhydrazone of 5-hexen-2-one (0.665 g, 2.5 mmol) was reduced in $CDCl_3$ (6 mL) by CB (0.417 mL, 3.75 mmol). An internal standard, n-decane (0.390 mL, 2.0 mmol), was added. The CB was added at 0° and the solution stirred for 1 hr. $NaOAc \cdot 3H_2O$ was added and the solution heated to gentle reflux for 1 hr. GLC indicated a 97% yield of 1-hexene.

F. 2-Octanone Tosylhydrazone Reduction

1. BMS Reduction (Table VIII, page 36)

The tosylhydrazone of 2-octanone (4.44 g, 15 mmol), mp 96-98, NMR ($CDCl_3$, TMS): 8.00 and 7.40 (A_2X_2, 4H, Ar), 2.43 (s, 3H, CH_3-C_6H_4-), 2.17 (m, 2H, $-CH_2(CH_3)C{=}N-$), 1.77 (s, 3H, $-CH_2(CH_3)C{=}N-$), 1.17 (m, 8H, $-(CH_2)_4-$), 0.80 (m, 3H, $-(CH_2)_4CH_3$)) prepared via the method of Hutchins et al. [35], was dissolved in diglyme (38 mL) and cooled to -5°. BMS (1.19 mL, 12 mmol) was added slowly. An internal standard, n-undecane (1.48 mL, 7 mmol), was added. The reduction of the tosylhydrazone was followed by NMR. After 1.5 hr, NMR showed greater than 90% reduction. Portions of the reaction solution were removed and quenched using various reagents as indicated below.

a. HOAc Quenching. The reaction solution (5.43 mL, 1.84 mmol of reduced tosylhydrazone) was quenched with HOAc (3 mL, 52.4 mmol). After

sitting for 30-60 min, Na_2CO_3 was added to neutralize the acid. The mixture was extracted with ether; GLC analysis indicated only a trace of octane.

b. H_2O Quenching. The reaction solution (5.43 mL, 1.84 mmol of reduced tosylhydrazone) was quenched with water (0.20 mL, 10 mmol). After sitting for 30-60 min, GLC indicated a 25% yield of octane.

c. MeOH Quenching. The reaction solution (5.43 mL, 1.84 mmol of reduced tosylhydrazone) was quenched with methanol (1 mL, 5.7 mmol). After sitting for 30-60 min, GLC indicated a 46% yield of octane.

d. NaOAc in HOAc Quenching. The reaction solution (5.43 mL, 1.84 mmol of reduced tosylhydrazone) was quenched with anhydrous sodium acetate (0.205 g, 2.5 mmol) in acetic acid (1.0 mL). After sitting for 30-60 min, GLC indicated a 21% yield of octane.

e. NaOAc in $HO(CH_2)_2OH$ Quenching. The reaction solution (5.43 mL, 1.84 mmol of reduced tosylhydrazone) was quenched by first adding anhydrous sodium acetate (0.205 g, 2.5 mmol) followed by ethylene glycol (4.0 mL, 57.9 mmol). After sitting for 30-60 min, GLC indicated a 32% yield of octane.

f. $NaOCH_3$ in CH_3OH Quenching. The reaction solution (5.43 mL, 1.84 mmol of reduced tosylhydrazone) was quenched with a $NaOCH_3$ in CH_3OH (5 mL, 1.0 M). After sitting for 30-60 min, GLC indicated a 69% yield of octane.

g. $n\text{-}C_4H_9Li$ Quenching. The reaction solution (5.43 mL, 1.84 mmol of reduced tosylhydrazone) was quenched with n-butyl lithium (0.83 mL,

2.0 mmol). After sitting for 30 min, GLC indicated a 29% yield of octane.

2. 9-BBN Reduction (Table IX, page 37)

The tosylhydrazone of 2-octanone (1.77 g, 6.00 mmol) was dissolved in diglyme (14.4 mL) and cooled to -5° using a salt-ice bath. 9-BBN (0.683 g, 6.00 mmol) was dissolved in diglyme (17 mL) and added to the tosylhydrazone solution. The internal standard, n-undecane (0.633 mL, 3.0 mmol), was added. After the addition of 9-BBN, the solution was allowed to warm to room temperature; it remained at room temperature for approximately 10 hr. The reaction could not be followed by NMR. Aliquots were taken from the reaction solution and quenched with various reagents.

a. HOAc Quenching. The reaction solution (4 mL) was quenched with acetic acid (0.5 mL, 8.7 mmol). After sitting for 30-60 min, GLC indicated a 15% yield of octane.

b. $BH_3 \cdot S(CH_3)_2$ Quenching. The reaction solution (2.0 mL) was quenched with 0.20 mL of borane methyl sulfide. After sitting for 30-60 min, GLC indicated a 7.29% yield of octane.

c. H_2O Quenching. The reaction solution (4 mL) was quenched with water (0.5 mL, 27.8 mmol). After sitting for 30-60 min, GLC indicated a 9.18% yield.

d. $NaOCH_3$ in CH_3OH Quenching. The reaction solution (4 mL) was quenched using $NaOCH_3$ in CH_3OH (1 M). After sitting for 30-60 min, GLC indicated a 20.4% yield of octane.

3. CB Reduction (Table X, page 38)

a. $NaOCH_3$ in CH_3OH Quenching. TH20 (tosylhydrazone of 2-octanone, 0.740 g, 2.5 mmol) was dissolved in CH_2Cl_2 (6.0 mL). An internal

standard, n-undecane (0.211 mL, 1.00 mmol), was added. The solution was cooled to 0° and CB (0.333 mL, 2.63 mmol) was added; the solution was allowed to stir for 1.5 hr. An aliquot was withdrawn from the solution (1.0 mL) and quenched with 0.5 mL $NaOCH_3$ in CH_3OH (1.0 M). The yield of octane by GLC was 59%.

b. NaI Quenching. TH20 (0.740 g, 2.5 mmol) was dissolved in CH_2Cl_2 (5.0 mL). An internal standard, n-undecane (0.211 mL 1.0 mmol), was added. The solution was cooled to 0° and CB (0.333 mL, 2.63 mmol) was added. After 2.5 hr, NaI (0.344 g, 2.63 mmol) and DMSO (4.0 mL) were added. The solution was allowed to sit 24 hr before running the GLC analysis. By GLC, there was only a trace of octane produced.

c. NaOAc in HOAc Quenching. TH20 (0.740 g, 2.5 mmol) was dissolved in CH_2Cl_2 (15 mL). An internal standard, n-undecane (0.211 mL, 1.00 mmol), was added. The solution was cooled to 0° and CB (0.317 mL, 2.5 mmol) was added over a 10-min period. After sitting 2 hr at 0°, NaOAc (0.150 g, 2.50 mmol) dissolved in HOAc (0.143 mL, 2.50 mmol) was added to the reaction solution. By GLC, there was a 66% yield of octane.

d. $BF_3 \cdot O(C_2H_5)_2$ Quenching. TH20 (0.740 g, 2.50 mmol) was dissolved in CH_2Cl_2 (15 mL). An internal standard, tetradecane (0.260 mL, 1.00 mmol), was added. The solution was cooled to 0° and CB (0.317 mL, 2.5 mmol) was added over a 10-min period followed by $BF_3 \cdot O(Et)_2$ (0.312 mL, 2.5 mmol). Subsequently, $NaOAc \cdot 3H_2O$ (0.340 g, 2.50 mmol) was added in DMSO (6.0 mL) followed by DMF (4.0 mL). After sitting 2 days, NaOAc (0.340 g, 2.50 mmol) was again added; GLC indicated a 75% yield of octane.

e. $SnCl_4$ Quenching. TH20 (0.740 g, 2.5 mmol) was dissolved in CH_2Cl_2 (10.0 mL). An internal standard, n-undecane (0.211 mL, 1.00 mmol), was added followed by the addition of $SnCl_4$ (0.282 mL, 2.5 mmol) at 0°. After 25 min, CB (0.317 mL, 2.5 mmol) was added. After sitting at 0° for 18 min, $NaOAc \cdot 3H_2O$ (0.340 g, 2.5 mmol) was added. The solution was allowed to sit 2 days before analysis. GLC indicated approximately 10 products. There were three peaks appearing in the octane region. The peak corresponding to octane was only a trace amount.

f. $NaOAc \cdot 3H_2O$ Quenching. TH20 (0.740 g, 2.5 mmol), $NaOAc \cdot 3H_2O$ (1.02 g, 7.50 mmol), and n-undecane (0.211 mL, 1.00 mmol) were dissolved in CH_2Cl_2 (6.0 mL) and cooled to 0°. CB (0.301 mL, 2.5 mmol) was added dropwise. The solution was analyzed 2 days later by GLC. Octane was obtained in 87.0% yield. NMR did not detect the presence of an alkene.

G. 2-Octanone Tosylhydrazone Reduction in Various Solvents

1. In $CHCl_3$

TH20 (0.740 g, 2.50 mmol), $NaOAc \cdot 3H_2O$ (1.02 g, 7.50 mmol), and n-undecane (0.211 mL, 1.00 mmol) were mixed in $CHCl_3$ (6.0 mL). The solution was cooled to 0°. CB (0.333 mL, 2.63 mmol) was added and the solution was allowed to warm slowly to room temperature. After 24 hr at room temperature, GLC indicated a 91% yield of octane.

2. In CH_2Cl_2

TH20 was reduced in CH_2Cl_2. The result is given as the last entry in Table X, page 38. Also, see experimental section F experiment 3(f).

3. In THF

TH20 (0.740 g, 2.50 mmol) and $NaOAc \cdot 3H_2O$ (1.02 g, 7.50 mmol) were mixed in THF (10 mL) and cooled to 0°. CB (0.317 mL, 2.50 mmol) was added and the solution was allowed to warm slowly to room temperature. After 2 days, an internal standard, n-undecane (0.211 mL, 1.00 mmol), was added. GLC indicated a 78% yield of octane.

4. In Benzene

TH20 (0.740 g, 2.50 mmol), $NaOAc \cdot 3H_2O$ (1.02 g, 7.50 mmol), and n-undecane (0.211 mL, 1.0 mmol) were mixed in benzene (10 mL) and the solution was cooled to 6-10°. CB (0.317 mL, 2.50 mmol) was added and the solution was allowed to warm slowly to room temperature. After sitting 24 hr at room temperature, GLC indicated a 70% yield of octane.

5. In Ethyl Ether

TH20 (0.740 g, 2.50 mmol), $NaOAc \cdot 3H_2O$ (1.02 g, 7.50 mmol), and n-undecane (0.211 mL, 1.00 mmol) were mixed in ethyl ether and cooled to 0°. CB (0.317 mL, 2.5 mmol) was added and the ice bath was allowed to slowly warm to room temperature. The solution sat 2 days; GLC analysis indicated a 69% yield of octane.

H. Reduction of Various Tosylhydrazones Using CB

1. TH20

a. TH20 Yield. TH20 (0.740 g, 2.5 mmol) was dissolved in $CHCl_3$ (6.0 mL) and cooled to 0°. The internal standard, n-undecane (0.211 mL, 1.00 mmol), was added. CB (0.333 mL, 2.63 mmol) was added followed by

$NaOAc \cdot 3H_2O$ (1.02 g, 7.5 mmol). The solution was allowed to warm to room temperature and then heated to reflux for 1 hr. GLC indicated a 91% yield of octane.

b. TH20 Isolation. TH20 (15.64 g, 52.7 mmol) was dissolved in $CHCl_3$ (125 mL). The internal standard, n-undecane (5.27 mL, 25 mmol), was added. The solution was cooled to 0°, and CB (6.31 mL, 58 mmol) was added over a 5-min period. After allowing the solution to warm to room temperature, $NaOAc \cdot 3H_2O$ (21.1 g, 155 mmol) was added and the solution heated to gentle reflux for 2 hr. GLC indicated an 81.9% yield. The solution was filtered and octane distilled to give an 88.7% (4.38 g) recovery (bp 124-127°, lit. 121-123°) [67]. NMR ($CDCl_3$): 1.10 (m, 12H, $CH_3(CH_2)_6CH_3$), 0.70 (m, 6H, $CH_3(CH_2)_6CH_3$).

2. Cyclohexanone Tosylhydrazone

The tosylhydrazone of cyclohexanone (0.660 g, 2.5 mmol, mp 155-158°, lit. 156°) [68] was dissolved in $CHCl_3$ (6.0 mL) at 0°. The internal standard, n-undecane (0.211 mL, 1.00 mmol), was added. CB (0.333 mL, 2.63 mmol) was added, and the solution was allowed to stand at 0° for 20 min before the $NaOAc \cdot 3H_2O$ (1.02 g, 7.5 mmol) was added. The solution was warmed to room temperature for 1 hr followed by heating to gentle reflux for 3 hr. GLC indicated a 92% yield of cyclohexane.

3. 2-Methylcyclohexanone Tosylhydrazone

The tosylhydrazone of 2-methylcyclohexanone [0.415 g, 1.48 mmol, mp 112-114°, NMR ($CDCl_3$): 8.00 and 7.40 (A_2X_2, 4H, Ar), 6.43 (broad m, 1H, -NH), 2.43 (s, 3H, $-ArCH_3$), 1.77 (broad m, 9H, ring hydrogens), 1.0 (d, 3H, $-C_6H_9-CH_3$] prepared by the method of Hutchins et al. [35] was

dissolved in $CHCl_3$ (6.0 mL) and cooled to 0°. CB (0.333 mL, 2.63 mmol) was added and the solution stirred at 0° for 30 min. The internal standard, undecane (0.211 mL, 1.00 mmol), was added. The solution was heated to reflux for 1 hr. GLC indicated a 60.3% yield of methylcyclohexane. After sitting 24 hr at room temperature, GLC indicated the yield had gone from 60.3% to 77%.

4. 2-Norbornanone Tosylhydrazone

The tosylhydrazone of 2-norbornanone (0.695 g, 2.5 mmol, mp 194-196°, lit 205-207°) [35] was dissolved in $CHCl_3$ (10.0 mL) along with the internal standard, n-undecane (0.211 mL, 1.00 mmol), and cooled to 0°. CB (0.333 mL, 2.63 mmol) was added and the solution stirred for 30 min. $NaOAc \cdot 3H_2O$ (1.02 g, 7.5 mmol) was added to the solution and the solution was allowed to warm to room temperature followed by a 3-hr reflux. GLC indicated a yield of 63% norbornane. NMR indicated that no alkene was present.

5. Isophorone Tosylhydrazone

The tosylhydrazone of isophorone (0.765 g, 2.5 mmol, mp 142-144°, lit. 143.5-145°) [35] was dissolved in $CHCl_3$ (6.0 mL). CB (0.317 mL, 2.5 mmol) was added and allowed to stir for 20 min at room temperature. $NaOAc \cdot 3H_2O$ (1.02 g, 7.5 mmol) was added and the solution was stirred at room temperature for 48 hr. At this time, anisole (0.181 mL, 1.67 mmol) was added as an internal standard. NMR analysis indicated a 41% yield of 3,5,5-trimethylcyclohexene. GLC indicated only one peak and when trapped the IR confirmed the product as 3,5,5-trimethylcyclohexene. IR (neat): 3.45 (s), 6.15 (w), 6.90 (m), 7.35 (m), 7.69 (w),

8.75 (w), 10.12 (m), 11.22 (w), 11.92 (w), 12.72 (w), 14.17 (s), 14.90 (s), (wavelength in microns). The NMR spectrum of 3,5,5-trimethylcyclohexene was identical with Sadtler No. 23384. NMR (neat): 5.37 (m, 2H, -CH=CH-), 2.03 (broad m, 1H, =CH(CH_3)CH-), 1.67 (m, 2H, =CHCH_2-), 1.27 (m, 2H, -C(CH_3)$_2$$CH_2$C(H)($CH_3$)-), 0.87 (m, -C($CH_3$)$_2$- and -C(H)($CH_3$)-).

I. Reduction of α,β-Unsaturated Tosylhydrazones Using CB

1. trans-1-Phenyl-1-buten-3-one Tosylhydrazone

a. trans-1-Phenyl-2-butene Yield. The tosylhydrazone of trans-1-phenyl-1-buten-3-one (0.764 g, 2.5 mmol, mp 172-173°, lit. 183-185°) [34] was slurried in THF (10 mL). CB (0.574 mL, 5.25 mmol) was added followed by n-nonane (0.268 mL, 1.50 mmol) as an internal standard. The slurry was warmed for 1.2 hr (30°). NaOAc·$3H_2O$ (1.02 g, 7.50 mmol) was added and the solution refluxed for 1 hr. The product NMR spectrum did not correspond to cis-1-phenyl-2-butene [66]. However, the product NMR spectrum was identical to trans-1-phenyl-2-butene [66]. GLC analysis indicated a 73.2% yield of trans-1-phenyl-2-butene. NMR (neat): 7.10 (s, 5H, Ph), 5.47 (t, 2H, -CH=CH-), 3.23 (d, 2H, PhCH_2-), 1.63 (d, 2H, CH_3CH=CH-).

b. trans-1-Phenyl-2-butene Isolation. The tosylhydrazone of trans-4-phenyl-3-buten-2-one (9.87 g, 31.44 mmol) was slurried in THF (62 mL). CB (3.48 mL, 33.0 mmol) was added at 0°. Additional THF (80 mL) was added and the solution was warmed to room temperature and held for 2 hr. Additional THF (20 mL) was added and the solution was allowed to stir an additional 2.5 hr at room temperature. The

$NaOAc \cdot 3H_2O$ (13.0 g, 31.4 mmol) was added and the solution refluxed for 1.25 hr. The solution sat overnight. Water (200 mL) was added followed by salt to effect the separation of THF and water. Ethyl ether (25 mL) was used to extract the water layer. The organic layers were combined and dried with magnesium sulfate. The solvent was partially removed by fractional distillation. An internal standard, dichloromethane (1.45 mL, 22.6 mmol), was added to determine the amount of trans-1-phenyl-2-butene present in solution (1.20 g, 28.9% yield). The solvent was then filtered through silica gel and the solvent fractionally distilled from the product. The product was collected to give 0.748 g, 65.3% recovery. NMR (neat): 7.10 (s, 5H, Ph-), 5.47 (t, 2H, -CH=CH-), 3.23 (d, 2H, $PhC\underline{H}_2$-), 1.63 (d, 2H, $C\underline{H}_3CH$=CH-).

2. trans-Cinnamaldehyde Tosylhydrazone Reduction

The tosylhydrazone of trans-cinnamaldehyde (0.750 g, 2.5 mmol, mp 157-158°, lit 160-162°) [35] was dissolved in $CHCl_3$ (6.0 mL). CB (0.310 mL, 2.79 mmol) was added followed by THF (6.0 mL). An internal standard, n-undecane (0.211 mL, 1.00 mmol), was added. The solution was allowed to sit overnight and $NaOAc \cdot 3H_2O$ (1.02 g, 7.5 mmol) was added. The solution was allowed to reflux for several hours. The NMR spectrum of 3-phenyl-1-propene was identical to the product obtained, Sadtler No. 3248. GLC indicated a 53% yield of 3-phenyl-1-propene. NMR ($CHCl_3$, reaction mixture): aromatic obscured, 5.83 (complex m, =CH-), 5.03 (d, $=CH_2$), 3.37 (d, $PhC\underline{H}_2CH$=).

3. Mesityl Oxide Tosylhydrazone

The tosylhydrazone of mesityl oxide (0.658 g, 2.47 mmol, mp 106-111°, lit. 105-110°) [69], prepared via a known procedure [69], was dissolved in $CHCl_3$ (5.0 mL) and cooled to 0°. CB (0.277 mL, 2.63 mmol) was added. The solution was allowed to warm to room temperature and stir for approximately 2 hr. The $NaOAc \cdot 3H_2O$ (1.02 g, 7.5 mmol) was added and the solution refluxed for 1.25 hr. The internal standard, n-undecane (0.211 mL, 1.00 mmol), was added. The NMR spectrum of cis-4-methyl-2-pentene did not match the product obtained, Aldrich No. 1,24D. However, the NMR spectrum of trans-4-methyl-2-pentene was identical to the product obtained, Aldrich No. 1,24C. GLC indicated a 65% yield of trans-4-methyl-2-pentene. NMR ($CHCl_3$): 5.33 (m, 2H, $(CH_3)_2CHCH=CHCH_3$), 2.17 (m, 1H, $(CH_3)_2CHCH=CHCH_3$), 1.60 (m, 3H, $(CH_3)_2CHCH=CHCH_3$), 0.93 (d, 6H, $(CH_3)_2CHCH=CHCH_3$).

4. 1-Acetylcyclohexene Tosylhydrazone

a. Ethylidenecyclohexane. The tosylhydrazone of 1-acetylcyclohexene (0.730 g, 2.50 mmol, mp 112-114°, lit. 120-121.5°) [35] was dissolved in $CHCl_3$ (6.0 mL). CB (0.310 mL, 2.94 mmol) was added. An internal standard, n-undecane (0.211 mL, 1.00 mmol), was added. The solution was allowed to sit several hr followed by the addition of $NaOAc \cdot 3H_2O$ (1.02 g, 7.50 mmol). The solution was refluxed for several hours. GLC indicated a 77% yield of ethylidenecyclohexane. NMR (neat): 5.13 (q, 1H, $C_6H_{10}=CHCH_3$), 2.10 and 1.57 (m, 13H, $C_6H_{10}=CHCH_3$).

b. Ethylidenecyclohexane Isolation. The tosylhydrazone of 1-acetylcyclohexene (40.6 g, 0.139 mmol) was dissolved in $CHCl_3$ (50 mL). CB (16.0 mL, 0.152 mmol) was added at 0°. The solution was allowed to warm to room temperature and was held for 1 hr followed by the addition of $NaOAc \cdot 3H_2O$ (30.0 g, 0.221 mmol). The solution was refluxed for 1 hr and filtered through silica gel. It was partially evaporated using a fractionation column. An internal standard, ethyl ether (0.800 mL, 7.72 mmol), was added and NMR was used to determine the amount of ethylidenecyclohexane present in solution (4.33 g, 28.3% yield). The solvent was fractionally distilled from the product which was then collected to give 3.80 g, 88% recovery (bp 132-133° at 743 mm, lit. 133-135°) [70].

5. Isophorone Tosylhydrazone

a. 3,5,5-Trimethylcyclohexene. The tosylhydrazone of isophorone (0.768 g, 2.5 mmol) was dissolved in $CHCl_3$ (6.0 mL) at 0°. CB (0.31 mL, 2.75 mmol) was added and the reduction allowed to proceed for 1 hr. The $NaOAc \cdot 3H_2O$ (1.02 g, 7.5 mmol) was added and the reaction mixture was refluxed for 1 hr. The internal standard, anisole (0.145 mL, 1.33 mmol), was added. NMR analysis indicated a 66% yield of 3,5,5-trimethylcyclohexene.

b. 3,5,5-Trimethylcyclohexene-3-d. The tosylhydrazone of isophorone was treated as in (5a) except $NaOAc \cdot 3D_2O$ (1.02 g, 7.18 mmol) was used in place of $NaOAc \cdot 3H_2O$. $NaOAc \cdot 3D_2O$ was prepared by dissolving anhydrous NaOAc in excess hot D_2O. The crystalline material that precipitated on cooling was dried and used "as is." The crystalline

solid was assumed to be $NaOAc \cdot 3D_2O$. The yield of 3,5,5-trimethylcyclohexene-3-d was 66% by NMR. The product was isolated using preparative GLC. IR (neat): 3.45 (s), 4.79 (w), 6.15 (w), 6.90 (m), 7.37 (m), 7.80 (w), 8.85 (w), 10.12 (m), 11.10 (w), 11.62 (w), 14.19 (w), 14.42 (m), 15.02 (m), (wavelength in microns). NMR ($CDCl_3$): 5.47 (m, 2H), 1.73 (m, 2H), 1.47 (m, 1H), 1.35 (m, 1H), 0.92 (m, 9H). Mass spectrum (70 eV) m/e (rel. intensity) 125 (48, M^+), 110 (100), 69 (74), 56 (33).

6. Cholest-4-en-3-one Tosylhydrazone

a. Cholest-4-en-3-one Tosylhydrazone Yield. The tosylhydrazone of cholest-4-en-3-one (1.43 g, 2.5 mmol, mp 131-132.3, lit. 142°) [52] prepared by the method of Hutchins et al. [35] was dissolved in $CHCl_3$ (6.0 mL) along with the internal standard, anisole (0.145 mL, 1.34 mmol). CB was added at 0°. The solution was warmed to room temperature and was held for an hour. $NaOAc \cdot 3H_2O$ (1.02 g, 7.50 mmol) was added and the solution heated to reflux for 1 hr. NMR indicated a 98% yield.

b. Cholest-4-en-3-one Tosylhydrazone Isolation. The tosylhydrazone of cholest-4-en-3-one (1.43 g, 2.5 mmol) was dissolved in $CHCl_3$ (6.0 mL) at 0°. CB (0.320 mL, 3.00 mmol) was added and the reduction allowed to proceed for 2 hr. $NaOAc \cdot 3H_2O$ (1.02 g, 7.5 mmol) and $CHCl_3$ (8.0 mL) were added. The solution was stirred for 0.5 hr and then heated to reflux for 1 hr. The slurry was filtered and the $CHCl_3$ removed by vacuum to give 1.055 g of residue. The residue was chromatographed over 20 g of alumina with hexane to give 820 mg of colorless viscous oil (89%). TLC indicated predominantly one product with a trace of starting material. An analytical sample (600 mg) was

obtained by further chromatography over 40 g of alumina. Mass spectrum M^+ 370 ($C_{27}H_{46}$); $[\alpha]_D$ +19.6; IR 831, 783, and 678 cm^{-1}; NMR (CCl_4): 0.66 (s, 3H, C-18, $-CH_3$), 0.95 (s, 3H, C-19, $-CH_3$), 5.23-5.75 (m, 2H, J=11 Hz, vinyl). The oily product crystallized after long standing, mp 48-50°. The literature values for 5-α-cholest-3-ene gave the following: $[\alpha]_D$ + 19.0 [71]; IR 771 and 671 cm^{-1} [72]; NMR: 0.66 (s, 3H, C-18, $-CH_3$), 0.94 (s, 3H, C-19, $-CH_3$), 5.39 (m, 2H, J=9.9 Hz, vinyl) [72]; mp 78-79° [73]. The literature values for 5-β-cholest-3-ene gave the following: $[\alpha]_D$ + 62 [72]; IR 832, 783, 680 cm^{-1} [72]; NMR: 0.66 (s, 3H, C-18, $-CH_3$), 0.94 (s, 3H, C-19, $-CH_3$), 5.43 (m, 2H, J=11 Hz, vinyl) [72]; mp 48-49° [71]. Thus, the product was identified as 5-β-cholest-3-ene.

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APPENDIX

TABLE XV

REACTION OF 2-METHYL-2-PROPANOL WITH CB[a]

Time (min)	% Reaction[b]
5	66.5
10	78.5
15	82.4
35	90.1
45	91.9
60	92.8
95	95.5
170	96.7

[a]The reaction was run by adding 5.25 mmol CB to 5.00 mmol of 2-methyl-2-propanol in 10 mL of $CHCl_3$.

[b]The % reaction was determined by comparing the amount of gas evolved (corrected to STP) to the theoretical amount for 5.00 mmol.

TABLE XVI

REACTION OF 2-PROPANOL WITH CB[a]

Time (min)	% Reaction[b]
10	74.6
20	81.6
30	85.9
50	88.7
75	91.7
175	94.6

[a]The reaction was run by adding 5.25 mmol of CB to 5.00 mmol of 2-propanol in 10 mL of $CHCl_3$.

[b]The % reaction was determined by comparing the amount of gas evolved (corrected to STP) to the theoretical amount for 5.00 mmol.

TABLE XVII

REACTION OF ETHANOL WITH CB[a]

Time (min)	% Reaction[b]
5	48.3
14	66.1
37	79.3
47	81.2
60	84.0
70	84.7
75	85.9
100	87.8
147	90.9
185	92.0
260	94.3

[a]The reaction was run by adding 5.25 mmol of CB to 5.00 mmol of ethanol in 10 mL $CHCl_3$.

[b]The % reaction was determined by comparing the amount of gas evolved (corrected to STP) to the theoretical amount for 5.00 mmol.

TABLE XVIII

REACTION OF METHANOL WITH CB[a]

Time (min)	% Reaction[b]
5	17.7
10	48.5
20	59.6
25	63.1
34	66.6
49	72.0
55	73.5
70	76.6
84	77.6
364	87.0

[a]The reaction was run by adding 5.25 mmol of CB to 5.00 mmol of ethanol in 10 mL of $CHCl_3$.

[b]The % reaction was determined by comparing the amount of gas evolved (corrected to STP) to the theoretical amount for 5.00 mmol.

TABLE XIX

REDUCTION OF HEPTANAL BY CB IN VARIOUS SOLVENTS

Time (min)	$CHCl_3$[a,b,c]	$CHCl_3$[c,d,e]	C_6H_6[c,f,d]	THF[c,g,h]
2	--	--	--	40.2
4	--	65.0	--	--
15	--	--	--	55.0
30	--	80.4	90.9	--
45	53.5	--	--	--
60	--	--	--	72.6
73	--	87.3	--	--
120	--	--	--	82.6
165	--	91.0	--	--
175	76.9	--	--	--
180	--	--	96.8	86.5
209	--	94.0	--	--
295	86.3	--	--	--
320	--	97.0	--	--
420	96.0	--	--	--
1410	--	98.0	--	--

[a]The reaction was run by adding 2.63 mmol of CB to 2.50 mmol of heptanol in 5.0 mL of $CHCl_3$.

[b]The reduction was followed by NMR by monitoring the formation of the borate ester relative to the protons of the starting material.

[c]The numbers in the given column indicate the percent reduction of heptanal in the designated solvent to give the corresponding heptoxy borate.

TABLE XIX (continued)

[d]The reaction was run by rapidly adding 5.25 mmol CB to 5.00 mmol of heptanal in 10 mL of $CHCl_3$.

[e]The reduction was followed by GLC by monitoring the disappearance of heptanal compared to the internal standard n-undecane.

[f]The reaction was run by adding 2.61 mmol CB to 2.61 mmol heptanal in 5.0 mL $CHCl_3$.

[g]The reaction was run by adding 2.50 mmol CB to 2.5 mmol heptanal in 5.0 mL THF.

[h]The reaction was followed by GLC by monitoring the disappearance of heptanal compared to the internal standard n-undecane.

TABLE XX

REDUCTION OF BENZALDEHYDE BY CB IN $CHCl_3$

Time (min)	% Reduction ($CHCl_3$)[a,b]	% Reduction ($CHCl_3$)[b,c]
15	29.6	--
40	--	82.8
42	63.6	--
64	58.6	--
95	--	91.7
130	84.6	--
315	88.3	--
335	--	87.1
540	85.0	--
1100	--	105

[a]The reaction was run by adding 2.63 mmol CB to 2.5 mmol benzaldehyde in 5.0 mL $CHCl_3$.

[b]The reduction was followed by NMR by monitoring the formation of the borate ester compared with the internal standard toluene.

[c]The reaction was run by adding 5.25 mmol CB to 2.5 mmol benzaldehyde in 10 mL $CHCl_3$.

TABLE XXI

REDUCTION OF CYCLOHEXANONE BY CB IN VARIOUS SOLVENTS

Time (hr)	$CHCl_3$[a,b,c]	Toluene[d,e]	THF[c,e,f]
0.500	35.8	67.7	45.0
0.830	--	--	52.4
1.00	--	68.6	--
2.00	--	83.5	64.0
2.92	63.3	--	--
3.25	--	79.8	--
4.00	--	--	66.0
4.25	74.0	83.6	--
5.42	71.5	--	--
6.00	--	--	81.0
9.00	--	--	85.0
10.10	83.0	--	--
20.40	--	95.6	--
21.70	83.6	--	--
23.50	--	--	92.0
25.30	--	91.0	--
35.5	--	--	94.0

[a]The reaction was run by adding 2.63 mmol CB to 2.5 mmol cyclohexanone in 5.0 mL $CHCl_3$.

[b]The reduction was followed by NMR by monitoring the formation of the borate ester compared with the internal standard CH_2Cl_2.

[c]The numbers in the given column indicate the percent reduction of cyclohexanone in the designated solvent to give the corresponding cyclohexoxy borate.

TABLE XXI (continued)

[d]The reaction was run by adding 2.63 mmol CB to 2.5 mmol cyclohexanone in 5.0 mL toluene.

[e]The reduction was followed by NMR by monitoring the formation of the borate ester compared with the internal standard 1,2-dichloroethane.

[f]The reaction was run by adding 2.63 mmol CB to 2.5 mmol cyclohexanone in refluxing THF.

[g]The reduction was followed by GLC by monitoring the rate of disappearance of cyclohexanone compared to the internal standard n-undecane.

TABLE XXII

REDUCTION OF 2-METHYLCYCLOHEXANONE BY CB IN $CHCl_3$[a]

Time (hr)	% Reduction[b]
2.00	47.6
10.30	68.3
21.30	79.7
45.80	87.4
142.00	92.9

[a]The reaction was run by adding 2.63 mmol CB to 2.5 mmol 2-methylcyclohexanone in 5.0 mL $CHCl_3$.

[b]The reduction was followed by NMR by monitoring the formation of the borate ester compared to the ring and methyl protons of the starting material and product.

TABLE XXIII

REDUCTION OF 4-t-BUTYLCYCLOHEXANONE BY CB IN $CHCl_3$[a]

Time (hr)	% Reduction[b]
4.5	49.2
45.3	49.0

[a]The reaction was run by adding 2.79 mmol CB to 2.66 mmol 4-t-butylcyclohexanone in 5.0 mL $CHCl_3$.

[b]The reduction was followed by NMR by monitoring the formation of the borate ester compared to ring and t-butyl protons of the starting material and product.

TABLE XXIV

REDUCTION OF THE TOSYLHYDRAZONE OF 2-OCTANONE BY CB IN $CHCl_3$[a]

Time (min)	% Reduction[b]
7	17.0
30	60.4
39	87.0
55	100.0

[a]The reaction was run by adding 2.63 mmol CB to 2.50 mmol 2-octanone tosylhydrazone in 5.0 mL $CHCl_3$.

[b]The reduction was followed by NMR by monitoring the disappearance of the methyl group attached to the imine carbon relative to the benzylic methyl group.

TABLE XXV

REDUCTION OF THE unsym-DIMETHYLHYDRAZONE OF 2-OCTANONE BY CB IN $CHCl_3$[a]

Time (min)	% Reduction[b]
6.0	33.3
20.0	46.7
34.0	75.8
43.0	91.6
50.0	93.5
60.0	93.2

[a]The reaction was run by adding 2.63 mmol CB to 2.5 mmol unsymmetrical-dimethylhydrazone of 2-octanone in 5.0 mL $CHCl_3$.

[b]The reduction was followed by NMR by monitoring the disappearance of the methyl group attached to the imine carbon relative to the N-methyl groups.

TABLE XXVI

REDUCTION OF DIMETHYL SULFOXIDE BY CB IN $CHCl_3$[a]

Time (min)	% Reduction[b]
0.333	43.0
1.58	78.8
2.33	80.2
2.83	80.7
5.33	81.5
18.3	91.4
23.8	92.7
40.3	97.3

[a]The reaction was run by adding 5.26 mmol CB to 2.5 mmol dimethyl sulfoxide in 5.0 mL $CHCl_3$.

[b]The reduction was followed by NMR by monitoring the appearance of the dimethyl sulfide compared to the internal standard anisole.

TABLE XXVII

REDUCTION OF TRIMETHYLAMINE-N-OXIDE BY CB IN $CHCl_3$[a]

Time (min)	% Reduction[b]
0.217	77.6
0.517	83.0
0.800	89.0
1.20	91.1
3.00	92.2
8.45	94.0
20.50	94.0

[a]The reaction was run by adding 5.26 mmol CB to 2.5 mmol trimethylamine-N-oxide in 5.0 mL $CHCl_3$.

[b]The reduction was followed by NMR by monitoring the disappearance of trimethylamine-N-oxide compared to the internal standard anisole.

TABLE XXVIII

REDUCTION OF n-BUTYRIC ANHYDRIDE BY CB IN $CHCl_3$[a]

Time (hr)	% Reduction[b]
0.5	41.2
2.0	54.0
3.25	63.6
4.17	68.0
11.8	74.5
19.1	79.5

[a]The reaction was run by adding 10.7 mmol CB to 2.5 mmol n-butyric anhydride in 5.0 mL $CHCl_3$.

[b]The reduction was followed by NMR by monitoring the disappearance of the methylene hydrogens to the acyl carbon compared to hydrogens on the carbon in the borate ester ($-CH_2-O-B=$).

TABLE XXIX

REDUCTION OF PROPYLENE OXIDE BY CB IN $CHCl_3$

Time (hr)	% Reduction[a,b]	% Reduction[c,d]
0.450	--	92.7
0.617	34	--
1.00	--	100
2.38	46	--
3.75	56	--
5.50	68	--
21.3	88	--
26.5	92	--

[a]The reaction was run by adding 2.5 mmol CB to 2.5 mmol propylene oxide in 5.0 mL $CHCl_3$.

[b]The reduction was followed by GLC by monitoring the disappearance of propylene oxide compared with the internal standard n-undecane.

[c]The reaction was run by adding 5.25 mmol CB to 2.5 mmol propylene oxide in 5.0 mL $CHCl_3$.

[d]The reduction was followed by NMR by monitoring the appearance of the two borate esters ($CH_3CH_2CH_2$-O-B=) and ($(CH_3)_2$CH-O-B=) compared to the starting material.

TABLE XXX

REDUCTION OF 1-HEXYNE BY CB IN VARIOUS SOLVENTS

Time (hr)	$CHCl_3$[a,b,c]	$CHCl_3$[c,d,e]	THF[b,c,f]	THF[c,g,h]
1.50	--	--	--	19.5
2.75	--	23.5	--	--
5.30	23.6	--	--	--
6.67	--	--	--	35.5
8.75	--	75.8	--	--
9.00	--	--	11.4	--
12.2	--	--	18.7	--
17.5	--	--	--	42.4
20.3	--	77.6	--	--
25.3	78.5	--	--	--
25.5	--	--	29.4	51.4
26.3	--	74.6	--	--
28.0	--	--	34.2	--
29.5	--	--	44.0	--
30.0	73.6	--	--	--
31.3	--	80.0	--	--
53.0	82.0	--	--	--
69.4	--	78.0	--	--
72.0	--	--	--	51.6
119	--	--	44.5	--

TABLE XXX (continued)

[a]The reaction was run by adding 2.63 mmol CB to 2.50 mmol 1-hexyne in 5.0 mL $CHCl_3$. The numbers represent percent yield.

[b]The reduction was followed by NMR by monitoring the appearance of the terminal vinylic hydrogen compared to the internal standard phenanthrene.

[c]The numbers in the given column indicate the percent reduction in the given solvent under the given conditions.

[d]The reaction was run by adding 2.63 mmol CB to 2.5 mmol 1-hexyne in 5.0 mL of refluxing $CHCl_3$.

[e]The reduction was followed by NMR by monitoring the appearance of the terminal vinylic hydrogen compared to the internal standard 1,2-dichloroethane.

[f]The reaction was run by adding 2.63 mmol CB to 2.50 mmol 1-hexyne in 5.0 mL THF.

[g]The reduction was run by adding 2.63 mmol CB to 2.50 mmol 1-hexyne in 5.0 mL refluxing THF.

[h]The reduction was followed by NMR by monitoring the appearance of the terminal vinylic hydrogen compared to the internal standard benzene.

TABLE XXXI

REDUCTION OF PROPIONIC ACID BY CB IN $CHCl_3$[a]

Time (hr)	% Reduction[b]
3.0	14.4
15.0	46.2
25.1	65.9
39.1	68.6
49.8	71.7
88.1	72.7

[a]The reaction was run by adding 7.88 mmol CB to 2.50 mmol propionic acid in 5.0 mL $CHCl_3$.

[b]The reduction was followed by NMR by monitoring the formation of the borate ester compared to the hydrogens to the acyl carbon.

TABLE XXXII

REDUCTION OF CYCLOPENTANONE BY CB IN VARIOUS SOLVENTS

Time (hr)	% Reduction ($CHCl_3$)[a,b]	% Reduction (THF)[c,d]
1.17	15.9	--
2.10	17.7	--
3.17	--	7.00
4.00	--	25.0
11.1	35.9	--
15.8	41.6	--
20.1	--	39.2
22.3	41.8	--
24.5	--	52.0
27.2	--	46.2
35.1	52.7	--
49.8	62.4	--
62.0	61.3	--
72.1	67.9	--
79.0	--	73.8
87.5	66.9	--

[a]The reaction was run by adding 2.63 mmol CB to 2.50 mmol cyclopentanone in 5.0 mL $CHCl_3$.

[b]The reduction was followed by NMR by monitoring the rate of formation of the borate ester compared to the ring hydrogens.

[c]The reaction was run by adding 2.63 mmol CB to 2.50 mmol cyclopentanone in 5.0 mL $CHCl_3$.

[d]The reduction was followed by GLC by monitoring the disappearance of cyclopentanone compared to the internal standard n-dodecane.

TABLE XXXIII

REDUCTION OF 2-OCTANONE BY CB IN $CHCl_3$

Time (hr)	% Reduction[a,b]	% Reduction[c,d]
0.50	--	18.3
2.75	--	37.0
2.83	17.5	--
6.33	--	56.0
7.50	23.0	--
18.8	33.0	--
26.4	41.0	75.0
32.2	48.0	--
49.3	--	80.0
47.8	54.0	--
71.8	--	91.0
98.3	--	92.0
139	67.0	--
163	70.0	--

[a]The reaction was run by adding 2.63 mmol CB to 2.50 mmol 2-octanone in 5.0 mL $CHCl_3$.

[b]The reduction was followed by NMR by monitoring the rate of formation of the borate ester compared to the internal standard CH_2Cl_2.

[c]The reaction was run by adding 5.25 mmol CB to 2.5 mmol 2-octanone in 5.0 mL $CHCl_3$.

[c]The reduction was followed by NMR by monitoring the rate of formation of the borate ester compared to the internal standard CH_2Cl_2.

TABLE XXXIV

REDUCTION OF ACETYL CHLORIDE BY CB IN $CHCl_3$[a]

Time (hr)	% Reduction[b]
0.917	11.0
2.28	11.9
10.9	15.1
15.8	15.5
22.4	16.4
49.6	16.0
62.0	17.8
72.2	19.5

[a]The reaction was run by adding 10.5 mmol CB to 5.00 mmol acetyl chloride in 5.0 mL in $CHCl_3$.

[b]The reduction was followed by NMR by monitoring the rate of formation of the borate ester compared to the methyl group of the product and starting material.

TABLE XXXV

REDUCTION OF PROPIONITRILE BY CB IN $CHCl_3$[a]

Time (hr)	% Reduction[b]
12.1	9.2
15.9	13.3
22.5	21.2
35.3	35.3
61.8	49.5
71.9	56.7
89.2	50.4

[a]The reaction was run by adding 10.5 mmol CB to 5.00 mmol propionitrile in 10 mL $CHCl_3$.

[b]The reduction was followed by NMR by monitoring the formation of the boron-amine derivative compared with the internal standard anisole.

TABLE XXXVI

REDUCTION OF N,N-DIMETHYLACETAMIDE BY CB IN $CHCl_3$

Time (hr)	% Reduction[a,b]	% Reduction[c,d]
1.58	14.7	--
5.75	24.2	--
6.08	--	41
11.7	--	56.9
12.6	28.3	--
22.1	--	63.0
30.0	27.6	--
35.7	24.5	--
49.4	27.0	--
60.7	--	70.0
77.3	--	75.0
84.6	34.7	--
94.3	--	74.1
102	40.0	--
150	--	72.0

[a]The reaction was run by adding 5.25 mmol CB to 2.50 mmol N,N-dimethylacetamide in 5.0 mL $CHCl_3$.

[b]The reduction was followed by NMR by monitoring the formation of N,N-dimethylethylamine compared with the protons present in the starting material.

[c]The reaction was run by adding 7.88 mmol CB to 2.5 mmol N,N-dimethylacetamide in 5.0 mL $CHCl_3$.

TABLE XXXVII

REDUCTION OF 1-OCTENE BY CB IN VARIOUS SOLVENTS

Time (hr)	$CHCl_3$[a,b]	THF[b,c]	THF[b,d,e]
0.50	--	3.00	7.4
1.00	--	--	8.5
1.17	2.66	--	--
2.00	--	6.00	13.4
3.00	--	6.50	20.3
4.00	--	7.50	18.9
4.85	3.40	--	--
17.5	--	8.70	60.4[e]
27.5	--	14.0	68.6
43.2	5.26	--	--
46.5	--	25.5	82.9
70.5	--	--	65.0
94.5	--	--	61.3

[a]The reaction was run by adding 2.5 mmol CB to 2.5 mmol 1-octene in 5.0 mL $CHCl_3$. The numbers represent % reduction in each column.

[b]The reduction was followed by GLC by monitoring the disappearance of 1-octene compared to the internal standard n-nonane.

[c]The reaction was run by adding 2.63 mmol CB to 2.5 mmol of 1-octene in 5.0 mL THF.

[d]The reaction was run by adding 2.63 mmol CB to 2.5 mmol 1-octene in 5.0 mL refluxing THF.

[e]By GLC, two peaks were present after 17.5 hr. One peak had the same retention time as 1-octene whereas the second peak had a retention time only slightly different (the peaks overlapped slightly). After 94.5 hr, the starting material had all but disappeared leaving the second peak.

TABLE XXXVIII

REDUCTION OF ETHYL BUTYRATE BY CB IN VARIOUS SOLVENTS

Time (hr)	% Reduction ($CHCl_3$)[a,b]	% Reduction (THF)[b,c]
1.00	--	21.8
4.17	--	32.1
7.17	21.0	44.5
18.2	26.1	66.7
25.8	30.9	67.6
31.2	32.5	69.1
41.5	34.1	72.9
65.0	40.1	--
68.0	--	71.3

[a]The reaction was run by adding 5.25 mmol CB to 2.50 mmol ethyl butyrate in 5.0 mL refluxing $CHCl_3$.

[b]The reduction was followed by GLC by monitoring the disappearance of ethyl butyrate compared to the internal standard n-nonane.

[c]The reaction was run by adding 5.25 mmol CB to 2.5 mmol ethyl butyrate in 5.0 mL refluxing THF.

TABLE XXXIX

REDUCTION OF TRIFLUOROACETIC ANHYDRIDE BY CB IN $CDCl_3$[a]

Time (hr)	% Reduction[b]
1.50	18.9
22.8	24.6
25.8	30.7
49.2	45.8
95.0	51.9

[a]The reaction was run by adding 1.94 mmol CB to 0.462 mmol trifluoroacetic anhydride in 1.0 mL $CDCl_3$.

[b]The reduction was followed by NMR by monitoring the appearance of the borate ester compared to the internal standard toluene.

VITA

John Dayton Baker, Jr., was born in Norton, Virginia, on 27 January 1949. He grew up in the shadow of Sheep Rock and graduated from Coeburn High School in 1967. The next four years were spent at Clinch Valley College of the University of Virginia, where he was awarded a trip to Germany by the language department and was a varsity letterman in both tennis and baseball. Symbolizing his efforts, he was awarded the B.A. in Chemistry. He worked in E.C.P.I. at Tennessee Eastman Company in the summer of 1971. In the fall of 1971, he entered the Graduate School of The University of Tennessee, where he held a teaching assistantship for three years and a research assistantship for one year.

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