$[Co(R\text{-}pn)_2\ (dabp)]^{3+}$, $[Co(R, R\text{-}chxn)_2\ (dabp)]^{3+}$, *cis*-α-[Co (2S, 9S-dimetrien) (dabp)]$^{3+}$, and *cis*-α-[Co(3S,8S-dimetrien)]$^{3+}$ gave one isomer each. The 2S,9S-dimetrien and 3S,8S-dimetrien are 2S,9S-dimethyltriethylenetetraamine and 3S,8S-dimethyltriethylenetetraamine.

In those bis(diamine)(dabp) Co complexes there are two possible diastereoisomers, $\Delta(\lambda\lambda\lambda)$ and $\Lambda(\lambda\lambda\lambda)$, though the $\Delta(\lambda\lambda\lambda)$ isomer is known to be more stable. The display of stereoselectivity in those cobalt(III) complexes has been attributed to the interactions between the hydrogens of dabp and the hydrogens of the tetradentate ligands or the hydrogens of the *cis-bis*(diamine). In those octahdral complexes. however, other influences from adjacent ligands and chelate rings give complications in determining stereoselectivity. The platinum (II) complexes designed in the present investigation have eliminated those influences in determining stereospecificity. Therefore the conformation of the dabp ligand in the square planar platinum complexes can be displayed with much greater certainty than in octahedral complexes.

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Reduction of Selected Carbonyl Compounds with 8-Oxyquinoline Dihydroboronite. Selective Reduction of Aldehydes in the Presence of Ketones

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8-Oxyquinoline dihydroboronite is prepared by mixing equimolar amounts of 8-hydroxyquinoline and borane-dimethyl sulfide complex in tetrahydrofuran at room temperature and its structure is determined by spectroscopic methods. The reagent is shown to be an extremely mild reducing agent and reduces aldehydes, cyclohexanones, and acid chlorides to some extent. The reagent in the presence of 0.1 equiv of boron trifluoride etherate in tetrahydrofuran at room temperature reduces selectively aldehydes in the presence of ketones, while the reagent in the presence of 1 equiv of boron trifluoride etherate rapidly reduces simple aldehydes and ketones but does not reduce carboxylic acids, esters, and amides.

Introduction

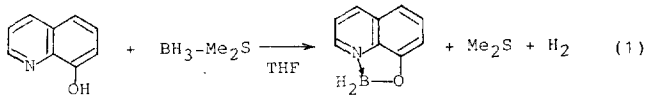
While amine-borane complexes have been extensively investigated as hydride reducing agents for a long time,[1] they failed to gain widespread use in synthetic organic chemistry, though they are remarkably stable and soluble in a variety of protic and aprotic solvents.[2] This is due in part to previous studies obtained with tertiary amine-borane and pyridine-borane complexes. These studies showed that tertiary amine-borane complexes in the absence of Lewis acid catalyst react with aldehyes and ketones very sluggishly even at elevated temperature, transferring only one of the three available hydrides. However, it has been recently reported that primary amine-borane complexes are somewhat different from tertiary amine-borane complexes as carbonyl reducing agents and can be utilized effectively for selective reductions.[3] Furthermore, amine-borane complexes derived from optically active amines,[4] sodium salts of optically active amino acids,[5] and methyl esters optically active amino acids have been utilized in asymmetric reduction of ketones. In contrast with many studies of amine-borane complexes, there are relatively few reports on amine-borane complexes with certain organic difunctional groups.[7]

As part of our research program directed toward the development of new hydride reducing agents,[8] we have recently communicated that aldehydes are selectively reduced to the corresponding alcohols in the presence of ketones with 8-oxyquinoline dihydroboronite in the presence of a catalytic amount of boron trifluoride etherate.[9] This paper describes a detail of reducing properties of a new hydride reducing agent,

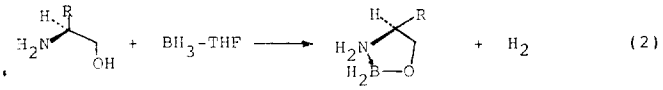
8-oxyquinoline dihydroboronite, in the reduction of selected carbonyl compounds.

Results and Discussion

The reagent was prepared by mixing equimolar amounts of 8-hydroxyquinoline[10] and borane-dimethyl sulfide complex in tetrahydrofuran at room temperature and the evolution of hydrogen gas was observed. The structure of the reagent was established by spectroscopic methods. The reagent exhibited a[11] BNMR with a triplet at +1.7 ppm (J_{BH} 125 Hz) with reference to boron trifluoride etherate and a strong IR absorption, due to the boron-hydrogen bond, at 2390 cm^{-1}. Thus, the structure of the reagent was assigned to 8-oxyquinoline dihydroboronite, containing a relatively rigid five-membered ring system as shown in eq. 1.[11]



(1)



(2)

Alkoxyamine-borane complexes, the similar types of reducing agents with 8-oxyquinoline dihydroboronite, has been utilized in the asymmetric reduction of aromatic ketones by Hirao[12] and was proposed to contain a relatively rigid five-membered ring system as shown in eq. 2. However, it has been recently reported that alkoxyamine-borane complexes disproportionate to various species, depending on the reaction conditions.[13] Unlike alkoxyamine-borane complexes, the reluctance of dispropotionation of 8-oxyquinoline dihydroboronite is of special interest in the utilization of the present reagent as a reducing agent.

The reagent was stable under a nitrogen atmosphere in a refrigerator for several weeks without any decomposition of hydride but it was readily decomposed in water and methanol with evolution of hydrogen gas. Facile decomposition of the reagent in protic solvents is in contrast with most amine-borane complexes.[4]

First, reducing properties of 8-oxyquinoline dihydroboronite toward selected carbonyl compounds were studied. As we expected from previously known results with tertiary amine-borane and pyridine-borane complexes,[1] the reagent exhibited an extremely mild reducing ability, The reduction was performed on several carbonyl compounds using equimolar amounts of the reagent and the substrate in tetrahydrofuran at room temperature and the reaction was monitered by GLC at appropriate intervals of time.

Reduction of nonyl aldehyde occurred very slowly, yielding only 10% of nonyl alcohol in 7 h. Likewise, 4-methylcyclohexanone, carvone, and acetophenone were reduced to the corresponding alcohols in 5%, 3%, and 1%, respectively. Furthermore, the reagent failed to reduce both caprylic acid and p-chlorobenzoic acid for 12 h at room temperature. The original acids were quantitatively recovered after usual workup. Similarly, methyl caprylate and methyl benzoate were not reduced at all for 24 h and the starting materials were recovered unchanged. Among several carbonyl compounds tested, acid chlorides were the most reactive toward the reagent but still the reaction occurred very slowly. Thus, the reaction of capryloyl chloride with an equimolar amount of the reagent at room temperature in 20 h afforded 20% of capryl alcohol along with 3% of capryl aldehyde.

TABLE 1: Selective Reduction of 3-Pentanone, 4-Methylcyclohexanone, and Nonyl Aldehyde with 8-Oxyquinoline Dihydroboronite in the Presence of Several Lewis Acids[a]

Lewis Acid	% Conversion to Alcohol[b]		
	A	B	C
$BF_3 \cdot Et_2O$	<1	46	>99
$ZnCl_2$	17	79	71
$AlCl_3$	1	17	34
$TiCl_4$	5	83	96
$SnCl_4$	14	63	95
$HgCl_2$	1	48	55

[a] The reduction was carried out in THF at room temperature for 7 h using total substrates, the reagent, and Lewis acid in a molar ratio of 1:1:0.1. [b] A,B, and C refer 3-pentanone, 4-methylcyclohexanone, and nonyl aldehyde, respectively.

Since no significant reduction of most carbonyl compounds with 8-oxyquinoline dihydroboronite in tetrahydrofuran at room temperature occurred and the reagent could not be applicable to reduction of carbonyl compounds by itself, we turned our attention to the possibility of increasing the reducing ability of the present reagent by addition of Lewis acid. In view of a wide use of boron trifluoride etherate in the literature for this purpose,[1,14] we examined the effectiveness of boron trifluoride etherate in the selective reduction of aldehydes in the presence of ketones.[15]

First, the reduction was carried out with an equimolar mixture of nonyl aldehyde, 4-methylcycohexanone, and 3-pentanone in the presence of boron trifluoride etherate in tetrahydrofuran at room temperature. It was found that the reagent in the presence of boron trifluoride etherate was a much more effective reducing agent. Not only was the rate of the reduciton drastically increased, but also the ability to distinguish between aldehydes and ketones was found. In the presence of 1 equiv of boron trifluoride etherate, the reduction was complete within 2 h, while in the presence of 0.03 equiv of boron trifluoride etherate, the reduction was not complete in 7 h, converting nonyl aldehyde and 4-methylcyclohexanone into the corresponding alcohols in 61% and 16%, respectively, without detectable reduction of 3-pentanone. After much experimentation, the best condition found for the highest selectivity between aldehydes and ketones was to employ 1 molar equiv of reagent and 0.1 equiv of eboron trifluorid etherate for each mole of the substrate. Uuder the present conditions, nonyl aldehyde was completely reduced into nonyl alcohol, while 46% conversion of 4-methylcyclohexanone into 4-methylcyclohexanol and no detectable reduction of 3-pentanone were observed.

In view of the fact that the reagent in the presence of 0.1 equiv of boron trifluoride etherate showed the possibility of

the selective reduction of aldehydes in the presence of acyclic ketones from the present study, we examined the relative effectiveness of several Lewis acids for this purpose. In general, the reduction was carried out using an equimolar mixture of substrates, the reagent, and Lewis acid in a molar ratio of 1:1:0.1 in tetrahydrofuran at room temperature for 7 *h* and the results are summarized in Table 1. Aluminum chloride showed very low catalytic effect due in part to its insolubility in tetrahydrofuran, while zinc chloride made 4-methylcyclohexanone slightly more reactive than nonyl aldehyde. Among several Lewis acids tested in this study, the reagent in the presence of titanium tetrachloride was the most effective reducing agent, though the selectivity between nonyl aldehyde and 3-pentanone achieved with titanium tetrachloride was somewhat lower than that with boron trifluoride etherate.

Since the results obtained with 0.1 equiv of boron trifluoride etherate among Lewis acids tested are the most encouraging, we have investigated several selective reductions of aldehydes in the presence of ketones to determine the scope and limitations of the present system. The experimental results are summarized in Table 2.

The reduction was performed on several structurally different aldehydes and ketones under almost same reaction conditions described previously. First, a competition between nonyl aldehyde and 3-pentanone resulted in a 99% reduction of nonyl aldehyde to nonyl alcohol with no detectable reduction of 3-pentanone as seen previously, while a competition beween benzaldehyde and 3-pentanone resulted in a 99% reduction of the aldehyde without detectable reduction of the ketone. Similar high selectivity was also obtained in the reduction of nonyl aldehyde in the presence of acetophenone, cyclopentanone, cycloheptanone, 2-octanone, and carvone. Furthermore, crotonaldehyde, α,β-unsaturated aldehyde, was selectively reduced into the crotonyl alcohol without detectable reduction of isophorone, α,β-unsaturated ketone. However, the present system reaches a limit with relatively reactive cyclohexanone derivatives. For example, reduction of an equimolar mixture of nonyl aldehyde and 4-methylcylohexanone gave a 90:28 mixture of nonyl alcohol and 4-methylcyclohexanol containing approximately 6:1 mixture of the *trans* and the *cis* isomer under the same reaction conditions. Furthermore, it is of interest to note that relatively reactive 4-methylcyclohexanone was selectively reduced to 4-methylcyclohexanol without detectable reduction of 3-pentanone under the present conditions.

We also examined two keto aldehydes using the substrate, the reagent, and boron trifluoride etherate in a molar ratio of 1:2:0.2 at room temperature for 7 h. 10-Oxopentadecanal was completely reduced to a mixture of 10-oxopentadecan-1-ol and 1,10-pentadecanediol in a ratio of 99:1 and 10-hydroxypentadecanal was not present in the reaction mixture. Similarly, in the reduction of *p*-bromophenacyl 6-oxohexanoate, the reduction of the ketone and the ester group was not detected. In each case the hydroxyketone was isolated in high yield after column chromatographic purification as shown below.

TABLE 2: Selective Reduction of Aldehydes with 8-Oxyquinoline in the Presence of $BF_3\cdot Et_2O$ in THF at Room Temperature for 7 h[a]

No.	Starting mixture	% Reduction[b]
1	Nonyl aldehyde	99
	3-Pentanone	<1
2	Nonyl aldehyde	93
	2-Undecanone	0
3	Nonyl aldehyde	98
	Cyclopentanone	1
4	Nonyl aldhyde	98
	Cycloheptanone	1
5	Nonyl aldehyde	95
	2-Octanone	0
6	Nonyl aldehyde	97
	Carvone	<1
7	Benzaldehyde	99
	3-Pentanone	<1
8	Benzaldehyde	99
	Acetophenone	0
9	Crotonaldehyde	95
	Isophorone	0
10	Nonyl aldehyde	90
	4-Methylcyclohexanone	28
11	4-Metthylcyclohexanone	71
	3-Pentanone	<1
12	4-Methylcyclohexanone	72
	Acetophenone	0

[a] Reduction was carried out with 1:1:2:0.2 molar ratio of the aldehyde, the ketone, the reagent, and $BF_3\cdot Et_2O$, respectively. [b] Determined by GLC using an internal standard.

$$CH_3(CH_2)_4CO(CH_2)_8CHO \longrightarrow CH_3(CH_2)_4CO(CH_2)_8CH_2OH$$
93% isolated yield

$$p\text{-Br-}C_6H_4COCH_2OCO(CH_2)_4CHO \longrightarrow p\text{-Br-}C_6H_4COCH_2OCO(CH_2)_4CH_2OH$$
90% isolated yield

Since the reagent in the presence of 1 equiv of boron trifluoride etherate was found to be a reactive reducing agent and reduced nonyl aldehyde, 4-methylcyclohexanone, and 3-pentanone to the corresponding alcohols within 2 h at room temperature, the reducing properties of the reagent in the presence of 1 equiv of boron trifluoride etherate were investigated in detail to determine the synthetic utility of the presenet system.

The reduction was carried out with an equimolar mixture of the substrate, the reagent, and boron trifluoride etherate in tetrahydrofuran at room temperature. Simple aldehydes and ketones such as benzaldehyde, acetophenone, 2-undecanone, and 4-*t*-butylcyclohexanone were reduced into the corresponding alcohols within 30 min. It is noteworthy that the reagent produced 91% of the thermodynamically more stable isomer from axial attack on 4-*t*-butylcyclohexanone along with 9% of the less stable isomer. However, reduction of relatively hindered ketones such as diisopropyl ketone and camphor occurred rather slowly and was not complete after 20 h. In the case of camphor, the products were found to contain 39% of the endo-alcohol and 45% of the exo-alcohol

TABLE 3: Reduction of Selected Carbonyl Compounds with Equimolar Amounts of 8-Oxyquinoline Dihydroboronite and $BF_3 \cdot Et_2O$ in THF at Room Temperature

Compounds	Time, h[a]	Products	Yield, %[b]
Nonyl aldehyde	0.2	Nonyl alcohol	86
Benzaldehyde	0.2	Benzyl alcohol	80
Cinnamyl aldehyde	0.2	Cinnamyl alcohol	90
Acetophenone	0.5	α-Methylbenzyl alcohol	98
2-Undecanone	0.5	2-Undecanonol	98
4-*t*-Butylcyclohexanone	0.3	4-*t*-Butylcyclohexanol	95[c]
2-Cyclohexen-1-one	1	2-Cyclohexen-1-ol	(65)
		Cyclohexanol	(35)
Diisopropyl ketone	20	2,4-Dimethylpentan-3-ol	(82)
		Diisopropyl ketone	(15)
Camphor	20	Borneol	(84)
		Camphor	(15)
Capryloyl chloride	10	Capryl alcohol	(28)
		Methyl caprylate	(70)[d]
Benzoyl chloride	10	Benzyl alcohol	(28)
		Methl benzoate	(70)[d]
Benzoic acid	10	Benzoic acid	80
Cinnamic acid	10	Cinnamic acid	96
Methyl benzoate	10	Methyl benzoate	72
Methyl 10-undecenoate	10	Methyl 10-undecenoate	96
N,N-Diethylcaprylamide	10	N,N-Diethylcaprylamide	97
N,N-Diethylbenzamide	10	N,N-Diethylbenzamide	98

[a] Not optimized. [b] The yields refer to isolated products. The numbers in parentheses indicate GLC yields. [c] The ratio of the *trans* and the *cis* isomer was 91:9. [d] The reaction mixture was quenched with methanol.

along with 15% of the unreacted camphor. Furthermore, reduction of 2-cyclohexen-1-one afforded a 65:35 mixture of 2-cyclohexen-1-ol and cyclohexanol.

The reagent in the presence of 1 equiv of boron trifluoride etherate failed to reduce carboxylic acids such as benzoic acid and cinnamic acid, carboxylic esters such as methyl benzoate and methyl 10-undecenoate, and tertiary amides such as N,N-diethylbenzamide and N,N-dietylcaprylamide. In all cases, the unreacted starting materials were essentially quantitatively recovered.

In its reducing properties toward selected carbonyl compounds, the reagent in the presence of 1 equiv of boron trifluoride etherate is shown to be a relatively mild reducing agent and comparable to sodium borohydride in some cases.

Experimental Section

Proton nuclear magnetic resonace spectra were obtaind on a Varian A-60 spectrometer and boron nuclear magnetic resonance spectrum was measured on a Varian CF-80A spectrometer using boron trifluoride etherate as a reference. Infrared spctra were taken on a Perkin-Elmer 267 spectrometer. Gas chromatographic analyses of product mixtures and purified samples were performed on a Varian 2800 gas chromatograph using 7 ft×0.125 in or 10 ft×0.125 in 10 % Carbowax stationary phase coated on Chromosorb W supporting material and nitrogen gas as a mobile phase.

Tetrahydrofuran was freshly distilled over sodium and benzophenone under a nitrogen atmosphere prior to use. Most of organic compounds utilized in this study were commercial products of the highest purity. Some compounds were synthesized by using known procedures. The products obtained were readily available materials in most cases. If not, identification was effected through alternate preparation by known procedures. All glasswares were dried in a drying oven and cooled under nitrogen. All reduction experiments were carried out under a nitrogen atmosphere, and hyperdermic syringes were used to transfer the solutions.

Since the reactions performed in this study are all similar in many respects, general procedures for typical reactions are described herein.

Preparation of a Standard Solution of 8-Oxyquinoline Dihydroboronite.

In a 100 m*l* flask with a magnetic stirring bar and a rubber septum was placed 8-hydroxyquinoline (3.63 g, 25 mmol). Under a dry nitrogen atmosphere, THF (45 m*l*) and borane-dimethyl sulfide complex (1.90 g, 25 mmol) were added to the flask in order at room temperature. The resulting solution was stirred at room temperature for 30 min to give approximately 0.5M solution of 8-oxyquinoline dihydroboronite in THF.[11] BNMR: δ+1.7 ppm (*t*, J_{BH} 125 Hz) IR: 2390 cm^{-1}.

General Procedure for Reduction of Carbonyl Compounds with 8-Oxyquinoline Dihydroboronite in the Absence of Lewis Acid. To a solution of a substrate (1.0 mmol) in THF (3 m*l*) at room temperature under nitrogen was added a solution of 8-oxyquinoline dihydroboronite (0.5*M*, 2.0 m*l*, 1.0 mmol) in THF. The reaction mixture was stirred at room temperautre for an appropriate time, quenched with water (0.5 m*l*), and analyzed with GLC. In the reduction of acid chlorides, the reaction mixture was quenched with methanol and stirred for 1 h to convert unreacted acid chlorides into the corresponding methyl esters.

General Procedure for Selective Reduction of Aldehydes with 8-Oxyquinoline Dihydroboronite in the Presence of 0.1 Equiv of $BF_3 \cdot Et_2O$. An aldehyde (1.0 mmol), a ketone (1.0 mmol), and an internal standard (1.0 mmol) were placed in a 25 m*l* flask with a magnetic stirring bar and a rubber septum under nitrogen. After THF (2 m*l*) was added at room temperature, a solution of 8-oxyquinoline dihydoboronite (0.5*M*, 4 m*l*, 2.0 mmol) in THF and a solution of $BF_3 \cdot Et_2O$ (0.1*M*, 2 m*l*, 0.2 mmol) in THF were added in order. The reaction mixture was stirred at room temperature for 7 h, quenched with water (0.5 m*l*), and analyzed with GLC.

Selective Reduction of p-Bromophenacyl 6-Oxohexanoate. To a solution of *p*-bromophenacyl 6-oxohexanoate (164 mg, 0.5 mmol) in THF (3 m*l*) at room temperature under nitrogen were added a solution of 8-oxyquinoline dihydroboronite (0.5*M*, 2 m*l*, 1.0 mmol) in THF and a solution of $BF_3 \cdot Et_2O$ (0.1*M*, 1 m*l*, 0.1 mmol) in THF. The resulting solution was stirred at room temperature for 7 h, quenched with water (0.5 m*l*) and THF was removed under reduced pressure. After methylene chloride (30 m*l*) was added to the flask, the reaction mixture was washed twice with 10% HCl

(20 m*l*). The aqueous layer was extracted with methylene chloride (20 m*l*). The combined methylene chloride solution was washed with water (20 m*l*) and saturated NaCl (20 m*l*), dried over anhydrous $MgSO_4$, filtered, and evaporated to dryness. The residue was subjected to silica gel column chromatography using hexane and ethyl ether (1:1) as an eluant to yield *p*-bromophenacyl 6-hydroxyhexanoate (148 mg) in 90% yield. The identity of the product was determined by independent synthesis.[16] NMR($CDCl_3$) δ 1.22–1.98 (*m*, 6H), 2.30–2.75 (*m*, 3H), 3.58 (*t*, 2H, J=5 Hz), 5.29 (*s*, 2H), 7.4–7.9 (*m*, 4H), IR($CHCl_3$) 3500, 1730, 1700 cm^{-1}. Selective reduction of 10-oxopentadecanal was carried out in a similar manner described above. Spectal data of 10-oxodecane-1-ol is as follows. NMR($CDCl_3$) δ 0.85–1.04 (*m*, 3H), 1.04–1.78 (*m*, 18H), 2.18–2.44 (*m*, 4H), 2.50 (*b,s*, 1H), 3.38–3.62 (*m*, 2H). IR($CHCl_3$) 3500, 1720 cm^{-1}.

General Procedure for Reduction of Carbonyl Compounds with Equimolar amounts of 8-Oxyquinoline Dihydroboronite and $BF_3 \cdot Et_2O$. To a solution of a substrate (1 mmol) in THF (2 m*l*) at room temperature under nitrogen were added a solution of 8-oxyquinoline dihydroboronite (0.5*M*, 2.5 m*l*, 1.3 mmol) in THF and a solution of $BF_3 \cdot Et_2O$ (1*M*, 1.3 m*l*, 1.3 mmol) in THF. The resulting solution was stirred at room temperature for an appropriate time and the reaction was monitored by tlc analysis. After the reaction mixture was quenched with water (0.5 m*l*), methylene chloride (30 m*l*) was added to the flask and the reaction mixture was washed twice with 10% HCl(20 m*l*). The aqueous layer was extracted with methylene chloride (20 m*l*) and the combined methylene chlorde solution was washed with water (20 m*l*) and saturated NaCl (20 m*l*), dried over anhydrous $MgSO_4$, filtered, and evaporated to dryness. In the cases of the products contaminated with 8-hydroxyquinoline, 8-hydroxyquinoline was completely removed by washing methylene chloride solution with saturated $CuSO_4$. In the reduction of acid chlorides, the reaction mixture was quenched with methanol instead of water. The products obtained in this study were characterized by spectral data (NMR, IR and GC) and by comparison with authentic samples. When several products were obtained, product mixtures were analyzed by GLC.

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