Modified Borohydride Agents, (1,4-Diazabicyclo[2.2.2]octane)(tetrahydroborato)zinc Complex $[Zn(BH_4)_2(dabco)]$. A New Ligand Metal Borohydride as a Stable, Efficient, and Versatile Reducing Agent

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(1,4-Diazabicyclo[2.2.2]octane)(tetrahydroborato)zinc complex is a stable compound which has been used for the selective reduction of aldehydes, ketones, α,β-unsaturated carbonyl compounds, α-diketones, acyloins and acyl chlorides to their alcohols and aldehydes in THF or CH_2Cl_2/hexane at room temperature or under reflux conditions.

Zinc, iron, and hydrogen sulfide are among the oldest reducing agents, having been used since the forties of the last century.[1] Catalytic hydrogenation[2] by Paul Sebatier in 1912 and reduction with metal hydrides,[3,4] especially sodium borohydride in 1943, by a research group headed by H. I. Schlesinger and including H. C. Brown, brought about a revolutionary change in the methodology for the reduction of functional groups in organic molecules.

The inability for a selective reduction of the carbonyl function of acids, amides, esters, and ketones in the presence of carbon double bonds by catalytic hydrogenation, has led to the wide-spread use of certain complex metal hydrides for reducing carbonyl groups.

Sodium borohydride ($NaBH_4$) and lithium aluminum hydride ($LiAlH_4$) are commonly used hydride transfer agents, which provide simple and convenient routes for the reduction of many organic functional groups, and are invariably used in organic synthesis.[1,4,5] However, in spite of their great convenience they suffer from certain limitations. Lithium aluminum hydride is an exceedingly powerful reducing agent capable of reducing practically all organic functional groups. Consequently, it is quite difficult to apply this reagent or the selective reduction of multifunctional molecules.[4] On the other hand, sodium borohydride is a remarkably mild reducing agent, and consequently is useful primarily for selective reductions of a few organic functional groups.[1,5]

These reagents represent two extremes of a possible broad spectrum. This situation made it desirable to develop means for controlling the reducting power of such reagents; such control could be achieved either by decreasing the reducing power of $LiAlH_4$ or by increasing that of $NaBH_4$. In fact, this has been achieved by different types of modifications, as summarized: (1) The substitution of one or more hydrides with other substituents to either increase (electron supplying group, i.e., alkyl, alkoxy) or temper (withdrawing group, i.e., CN, CO_2R) the hydride-delivering ability has attracted considerable interest over the years, and has supplied a wide range of boron hydride choices. Some examples are: $Na[(OAc)_3BH]$,[6,9] $Na[(OMe)_3BH]$,[10,11] sodium (dimethylamido) and (*t*-butylamido)trihydroborates,[6,12] $Na[(OAc)BH_3]$,[9,13] $Na[Et_3BH]$,[14] and $Na[CNBH_3]$.[15,16] (2) The variation in the alkali-metal cation and metal cation in the complex hydride would alter the reducing power of the resulting borohydrides. Some examples are: $LiBH_4$,[17—19] KBH_4,[20] $Ca(BH_4)_2$,[17,21] copper borohydride,[22—24] $Zn(BH_4)_2$,[25] $Zr(BH_4)_4$, $Ti(BH_4)_3$, and the others.[26] (3) A concurrent cation and hydride exchange has attracted increasing interest as an approach towards modifying the reducing ability of $NaBH_4$, and has played a key for further modifications. Some of these modified hydride reducing agents are: $K[(OAc)_3BH]$,[6,7] $Li[(OAc)_3BH]$,[27] $Li[Et_3BH]$ (superhydride),[28—30] $Li[BuBH_3]$,[31] lithium isopinocampheyl-9-borabicyclo[3.3.1]nonyl hydride (an optically active reagent)[32] (Fig. 1), lithium aminoborohydride (which is comparable in power to $LiAlH_4$ without having the dangerous properties of LAH,[33] lithium pyrolidinoborohydride,[34] lithium tri-*s*-butylborohydride (L-selectride)[35,36] and potassium tri-*s*-butylborohydride (K-selectride).[37] (4) The synthesis and structural studies of a few ligand-metal borohydrides $[L_xM(BH_4)_n]$ have been reported in the literature.[23,26,38—41] The use of the ligand (L_x) can induce considerable rela-

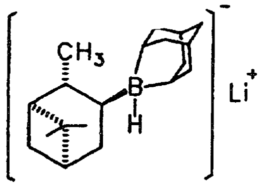


Fig. 1.

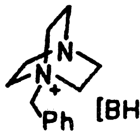


Fig. 2.

tive stabilities in these compounds compared to the parent metal borohydrides. The reactivity of the B–H bond can also be varied by the choice of the ligands on the metal ion.[26,38] Therefore, such modified tetrahydroborate complexes can constitute a class of reducing agents which could be useful for performing selective reductions of organic compounds. There are, however, very few reports in the literature on the use of such compounds as reducing agents in organic synthesis. Bis(triphenylphosphine)(tetrahydroborato)copper(I) $[Cu(BH_4)(Ph_3P)_2]$ is an example of one such reagent. It has been found that the BH_4^- moiety in this complex is deactivated to the extent that it only reduces acyl chlorides to the aldehydes, whereas $NaBH_4$ reduces them to their alcohols.[38,41] The other reported reagents in this category of compounds are μ-bis(cyanotrihydroborato)- tetrakis(triphenylphosphine)dicopper(I) $[Cu_2(BH_3CN)_2(Ph_3P)_4]$[40] and chlorobis(cyclopentadienyl)(tetrahydroborato)zirconium(IV) $[Zr(BH_4)(Cp)_2(Cl)]$.[39] They reflect the effects of the ligands and the type of cations. They show their own characteristic reactions with advantages over traditional hydride transfer agents. (5) By combining borohydrides with metals, metal salts, Lewis acids,[2] supports,[42] and mixed solvent systems, especially those containing methanol,[43] many different hydride transfer reductants have been introduced. With these new systems, chemo, regio, and stereoselective transformations have been successfully performed. (6) The first preparation of quaternary ammonium borohydrides was reported 40 years ago. Some of them show properties similar to alkali metal borohydrides, which offer no advantage as a synthetic reagent. Quaternary ammonium borohydrides with long-chain alkyl groups are suitable for different types of reductions in nonpolar solvents. Recently, we reported on the preparation of a new bulky quaternary ammonium borohydride (Fig. 2) which shows more selectivity than does its long-chain analogs for the reduction of different functional groups.[44,45]

Zinc tetrahydroborate ($Zn(BH_4)_2$) is a potential reducing agent, which has attracted much attention in the last decade. This reagent suffers from being unstable at room temperature and should always be used as its freshly prepared ethereal solution, even when it is supported on silica gel, it should be used on the same day of its preparation.[46,47] $Zn(BH_4)_2$ hydrolyzes vigorously when allowed to come into contact with water.[26] This compound is neutral[47] with a high coordination ability.[48] This reagent has effected very efficient chemo, regio, and stereoselective reductions.[48] Combination systems of $Zn(BH_4)_2$, e.g., $Zn(BH_4)_2$/*N*,*N*,*N*′,*N*′-tetramethylethylenediamine, $Zn(BH_4)_2/Me_3SiCl$, and $Zn(BH_4)_2/(CF_3CO)_2/DME$[49] have also been used for different reduction purposes. Recently, we reported on the preparation and use of polyvinylpyridine-supported zinc tetrahydroborate as a stable polymeric transition-metal borohydride reducing agent.[50] Even though this reagent is very stable it suffers from long reaction times and sometimes low yields of products. The other recently reported modified borohydrides are polyvinylpyridine-supported zirconium tetrahydroborate[51] and poly [tetrahydro[(1,4-η)pyrazine]boratozinc][52] $[Zn(BH_4)_2(pyz)]_n$ (Fig. 3). The latter is stable to heat and light, but explodes violently into flames when in contact with water.[53]

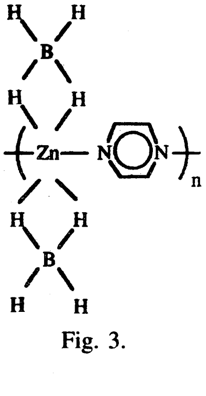


Fig. 3.

Recently, the preparation of tetrahydroboratozinc complexes with one and two molar ratios of 1,4-diazabicyclo-

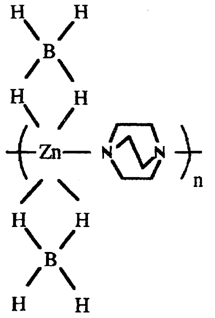
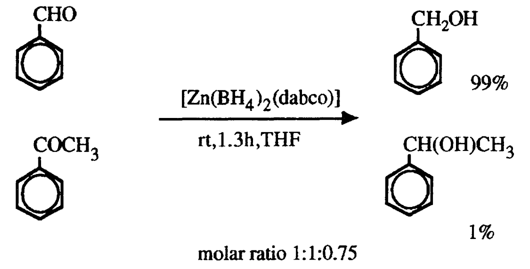
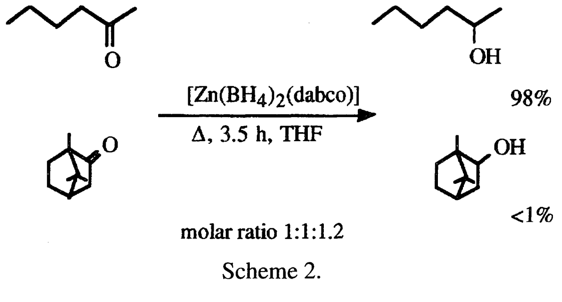


Fig. 4.

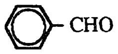
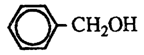
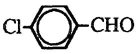
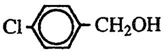
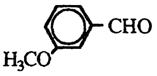
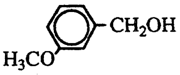
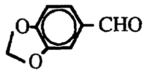
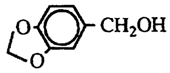
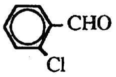
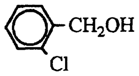
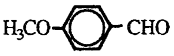
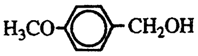
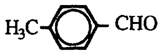
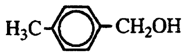
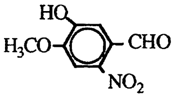
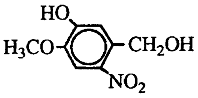
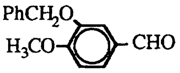
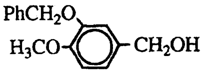
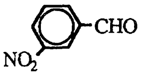
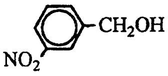
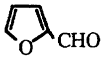
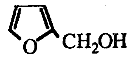
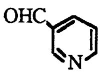
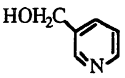
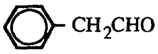
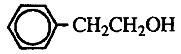
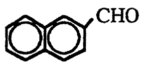
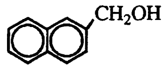
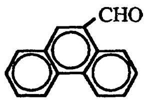
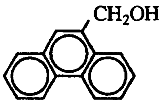
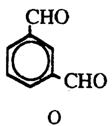
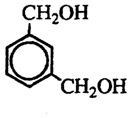
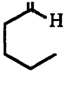
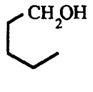
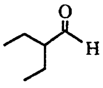
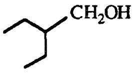


Scheme 1.



Scheme 2.

Table 1. Reduction of Aldehydes with $[Zn(BH_4)_2(dabco)]$[a]

Entry	Substrate	Product	Red/Subs	Time (h)	Conversion (%)	Yield (%)	Mp or bp (°C)[69]
1			0.75	0.7	100	90	205
2			0.75	0.4	100	97	70—72
3			0.75	1.3	100	97	250/723 mmHg
4			0.75	6.5	100	96	53—55
5			0.75	0.04	100	95	69—71
6			0.75	12	100	96	23—25
7			0.75	7	100	94	59—61
8			0.75	0.03	100	93	—
9			0.75	11	100	95	—
10			0.75	0.03	100	94	30—32
11			0.75	0.25	100	100[b]	170
12			0.75	0.25	100	100[b]	154/28 mmHg
13			0.75	2.7	100	95	219—221/750 mmHg
14			0.75	1.7	100	96	79—81
15			0.75	1	100	97	—
16			1.5	2.4	100	95	56—60
17			0.75	0.08	100	100[b]	136—138
18			0.75	1.7	100	100[b]	146

a) All reactions were performed in THF at room temperature. b) GC yield.

Table 2. Competitive Reduction of Aldehydes and Ketones with [Zn(BH$_4$)$_2$(dabco)]

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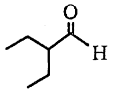
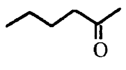
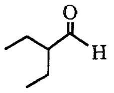
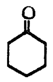
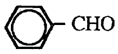
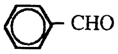
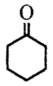
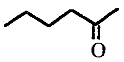
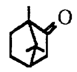
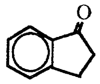
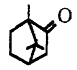
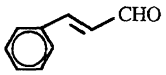
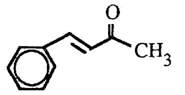
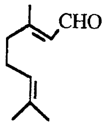
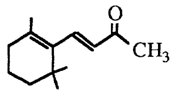
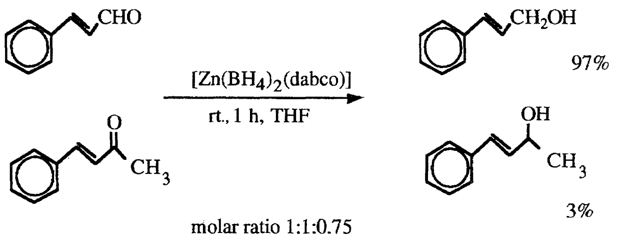
1			0.75 : 1 : 1	RT	2.7	95	9
2			0.75 : 1 : 1	RT	3.7	91	5
3			0.75 : 1 : 1	RT	1.5	99	1
4			0.75 : 1 : 1	RT	2	95	3
5			1.2 : 1 : 1	Reflux	3.5	98	< 1
6			1.2 : 1 : 1	Reflux	6.5	99	< 1
7			0.75 : 1 : 1	RT	3.5	97	3
8			1.5 : 1 : 1	RT	1	100	10

a) GC yield.



Scheme 3.

[2.2.2]octane (dabco) for studying their thermal and hydrolytic stabilities has been reported. The structures of the two complexes have been established as [Zn(BH$_4$)$_2$(dabco)] and [Zn(BH$_4$)$_2$(dabco)$_2$] by IR studies.[52b)] The heat and hydrolytic stabilities of these complexes encouraged us to investigate their reducing abilities for different types of functional groups in organic molecules.

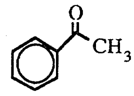
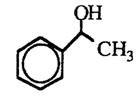
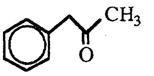
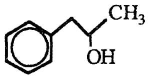
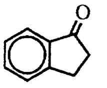
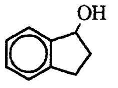
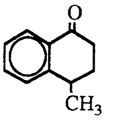
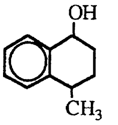
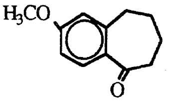
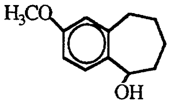
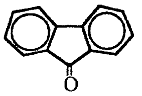
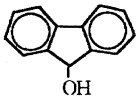
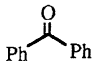
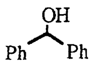
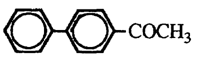
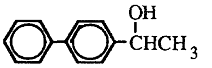
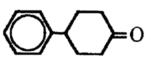
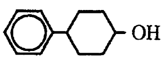
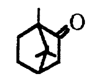
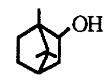
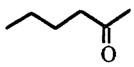
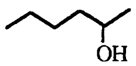
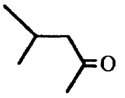
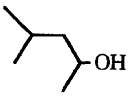
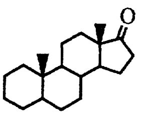
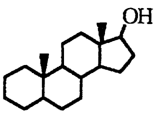
Results and Discussion

(1,4-Diazabicyclo[2.2.2]octane) (tetrahydroborato)zinc [Zn(BH$_4$)$_2$(dabco)] is a white stable compound which is prepared by the dropwise addition of one molar ethereal solution of 1,4-diazabicyclo[2.2.2]octane (dabco) to one molar ethereal solution of Zn(BH$_4$)$_2$[25)] at room temperature. The formation of the complex is very fast and the reagent is formed almost quantitatively. Filtration and drying of the precipitates resulted in a white fluffy powder which could be stored for months. The zinc percentage in the complex is determined by both gravimetric and atomic-absorption methods. The amount of [BH$_4$]$^-$ in this complex has been determined by an iodometric titration method.[54)] The measurements are consistent with the [Zn(BH$_4$)$_2$(dabco)] formula. The addition of two molar ratios of an ethereal solution of dabco in ether to a one molar ethereal solution of Zn(BH$_4$)$_2$ resulted in a compound with the molecular formula [Zn(BH$_4$)$_2$(dabco)$_2$]. Our preliminary studies concerning the reduction of carbonyl compounds with both regents show that [Zn(BH$_4$)$_2$(dabco)] is more reactive than [Zn(BH$_4$)$_2$(dabco)$_2$]. Therefore, we focused our attention on the former reagent during this study.

The solubility behavior of [Zn(BH$_4$)$_2$(dabco)] in various solvents such as THF, Et$_2$O, MeOH, EtOH, 2-propanol, *t*-BuOH, CH$_2$Cl$_2$, CH$_3$CN, and CHCl$_3$ was studied. The insolubility of this compound in these solvents may also offer the formation of a polymeric transition metal complex[55)] in which dabco acts as a metal–metal bridging ligand (Fig. 4). [Zn(BH$_4$)$_2$(dabco)] works efficiently as a reducing agent in aprotic solvents such as THF, CH$_3$CN, Et$_2$O, CHCl$_3$, and CH$_2$Cl$_2$. We have performed reactions in THF, which has a reasonable boiling point (when it is neccessary) and also a good solubilizing ability for structurally different organic molecules. The molar ratio of the reducing agent varies between 0.75—3 according to the nature of the carbonyl functional group in the molecules.

1. Reduction of Aldehydes and Ketones. The trans-

Table 3. Reduction of Ketones with $[Zn(BH_4)_2(dabco)]$[a)]

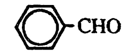
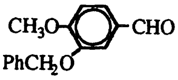
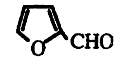
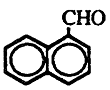
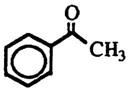
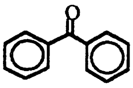
Entry	Substrate	Product	Red/Subs	Time (h)	Conversion (%)	Yield (%)	Mp or bp (°C)[69)]
1			1.2	5.4	100	92	204/745 mmHg
2			1.2	1.4	100	96	219—221
3			1.2	6	100	95	50—54
4			1.2	14	100	93	—
5			1.5	16	100	96	—
6			1.5	2.3	100	95	153—154
7			1.5	8.5	100	94	65—67
8			1.2	7.5	100	95	—
9			1.2	0.08	100	96	—
10			2.4	72	70	65	206—208
11			1.2	3.5	100	100[b)]	136
12			1.2	12	100	100[b)]	132
13			1.8	12	100	95	—

a) All reactions were performed in THF under reflux condition. b) GC yield.

formation of aldehydes and ketones to their alcohols is one of the most encountered reactions in the total synthesis of organic molecules. This goal could be easily achieved by $[Zn(BH_4)_2(dabco)]$ in THF either at room temperature or under reflux conditions. The selectivity of the reaction is temperature dependent. Aldehydes are reduced at room temperature in high yields (Table 1). In order to show the chemoselectivity of the reagent towards various carbonyl groups we performed the reduction of acetophenone in the presence of an equimolar amount of benzaldehyde with a reducing agent (0.75 mol) at room temperature. The selectivity ratio for the reaction of the aldehyde with respect to ketone is 99% (Scheme 1). This is a general trend for the reduction of various aldehydes in the presence of ketones with this reagent (Table 2).

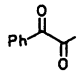
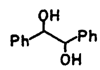
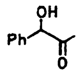
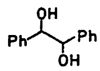
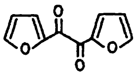
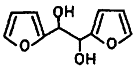
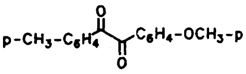
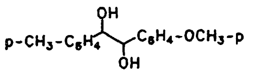
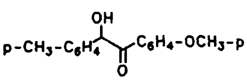
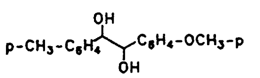
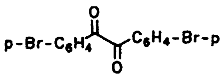
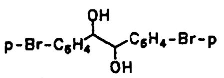
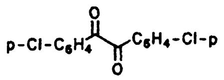
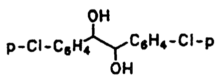
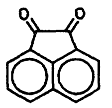
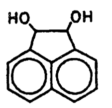
Ketones can be reduced in refluxing THF in 65—100% yields (Table 3). A higher molar ratio of the reducing agent is required for this reduction (1.2—1.5 mol) in comparison with that required for the reduction of aldehydes (0.75 mol). The bulky nature of the reagent induces a special steric

Table 4. Comparison of Reduction of Carbonyl Compounds to Their Corresponding Alcohols with $[Zn(BH_4)_2(dabco)]$, $[XP4\text{-}Zn(BH_4)_2]$,[a] $Zn(BH_4)_2$, BAAOTB,[b] and TBATB[c]

Entry	Substrate	$[Zn(BH_4)_2(dabco)]$		$[XP4\text{-}Zn(BH_4)_2]$[50]		$Zn(BH_4)_2$[48]		BAAOTB[44a]		TBATB[44b]	
		Molar ratio	Yield (%) (h)	Molar ratio	Yield (%) (h)	Molar ratio	Yield (%) (h)	Molar ratio	Yield (%) (h)	Molar ratio	Yield (%) (h)
1		0.75	100 (0.07)	1	80 (8)	1	100 (—)	1	90 (1)	4	96 (0.6)
2		0.75	97 (0.33)	1	95 (5)	1	100 (—)	1	90 (0.2)	—	—
3		0.75	96 (12)	1	75 (12)	—	—	2	85 (0.8)	—	—
4		0.75	95 (11)	1	72 (8)	—	—	2	90 (0.5)	—	—
5		0.75	100 (0.25)	1	83 (8)	—	—	1.5	90 (0.5)	—	—
6		0.75	96 (1.7)	1	84 (8)	—	—	1	90 (0.25)	—	—
7		1.2	92 (5.4)	2	0 (15)	1	0 (—)	2	80 (17)	4	98 (10)
8		1.5	94 (8.5)	2	0 (48)	—	—	2	90 (21.5)	—	—

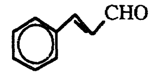
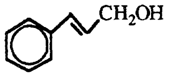
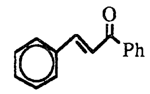
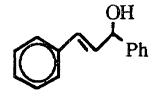
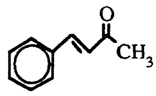
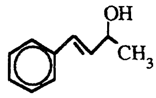
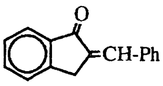
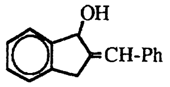
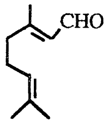
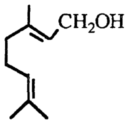
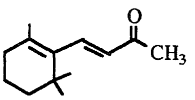
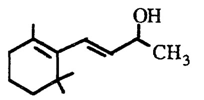
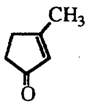
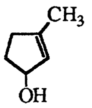
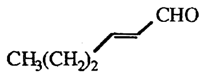
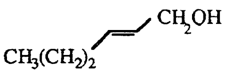
a) Cross-linked poly(4-vinylpyridine) supported zinc tetrahydroborate. b) 1-Benzyl-4-aza-1-azoniabicyclo[2.2.2]octane tetrahydroborate. c) Tetrabutylammonium tetrahydroborate.

Table 5. Reduction of α-Diketones and Acyloin Compounds with $[Zn(BH_4)_2(dabco)]$[a]

Entry	Substrate	Product	Red/Subs	Time (min)	Conversion (%)	Yield (%)	Mp or bp (°C)[59]
1			2	30	100	90	149—150
2			1	10	100	92	149—150
3			2	6	100	—	130—135 1 mmHg
4			2	40	100	90	125—126
5			1	25	100	91	125—126
6			2	10	100	94	242—243
7			2	10	100	93	—
8			2	20	100	92	203—208

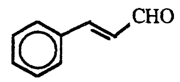
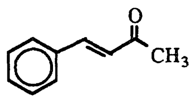
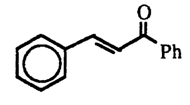
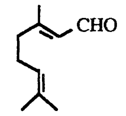
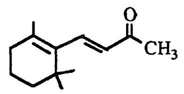
a) All reactions were performed in THF under reflux condition.

Table 6. Selective 1,2-Reduction of α,β-Unsaturated Aldehydes and Ketones with $[Zn(BH_4)_2(dabco)]$[a)]

Entry	Substrate	Product	Red/Subs	Time (h)	Conversion (%)	Yield (%)	Mp or bp (°C)[69]
1			0.75	4.5	100	94	33—35
2			1.3	7.5	100	95	—
3			1.2	2.2	100	92	144/21 mmHg
4			1.5	6	100	85	—
5			1.5	2.7	100	93	229—230
6			1.3	3	100	95	—
7			1.5	8	100	100[b)]	—
8			0.75	1.7	100	100[b)]	158—160

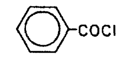
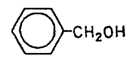
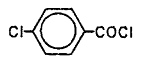
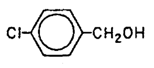
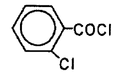
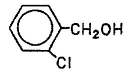
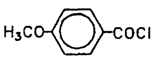
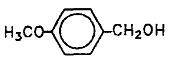
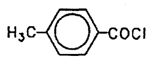
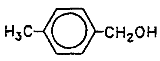
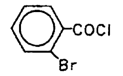
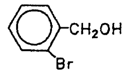
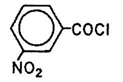
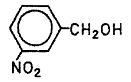
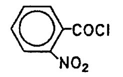
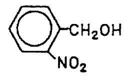
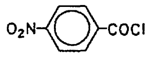
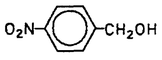
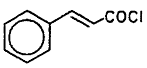
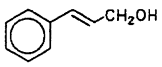
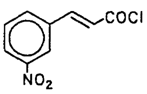
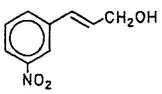
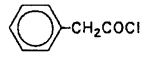
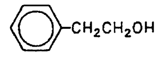
a) All reactions of aldehydes were performed at room temperature and for ketones under reflux conditions. b) GC yield.

Table 7. Comparison of 1,2-Reduction of α,β-Unsaturated Carbonyl Compounds to Their Corresponding Allylic Alcohols with $[Zn(BH_4)_2(dabco)]$, $[XP4\text{-}Zn(BH_4)_2]$,[a,b)] $Zn(BH_4)_2$, BAAOTB,[c)] and TBATB[d)]

Entry	Substrate	$[Zn(BH_4)_2(dabco)]$		$[XP4\text{-}Zn(BH_4)_2]$[50)]		$Zn(BH_4)_2$[48)]		BAAOTB[44a)]		TBATB[44b)]	
		Molar ratio	Yield (%) (h)	Molar ratio	Yield (%) (h)	Molar ratio	Yield (%) (h)	Molar ratio	Yield (%) (h)	Molar ratio	Yield (%) (h)
1		0.75	94 (4.5)	1	90 (9)	1	100 (0.5)	1	90 (0.33)	1	90 (0.13)
2		1.2	92 (2.2)	2	10 (15)	1	15 (30)	2	85 (0.4)	0.4	80 (0.4)
3		1.3	95 (7.5)	2	0 (24)	1	0 (—)	2	85 (3.2)	1	75 (3.3)
4		1.5	93 (2.7)	1	80 (18)	—	—	—	—	—	—
5		1.3	95 (3)	2	10 (15)	—	—	—	—	—	—

a) Unpublished results. b) Cross-linked poly(4-vinylpyridine) supported zinc tetrahydroborate. c) 1-Benzyl-4-aza-1-azoniabicyclo[2.2.2]-octane tetrahydroborate. d) Tetrabutylammonium tetrahydroborate.

Table 8. Reduction of Acyl Chlorides to Alcohols with [Zn(BH$_4$)$_2$(dabco)][a)]

Entry	Substrate	Product	Red/Subs	Time (h)	Conversion (%)	Yield (%)	Mp or bp (°C)[69)]
1			3	1	100	85	205
2			3	0.25	100	93	70—72
3			3	0.25	100	90	69—71
4			3	3.7	100	88	23—25
5			3	2.5	100	92	59—61
6			3	0.25	100	90	79—82
7			3	0.08	100	90	30—32
8			3	0.08	100	87	70—72
9			3	20	95	88[b)]	92—94
10			3	0.08	100	91	33—35
11			3	0.08	100	89	—
12			3	0.5	100	91	219—221 750 mmHg

a) All reactions were performed in THF at room temperature. b) This reaction was performed under reflux condition.

selectivity for the reduction of sterically hindered carbonyl groups. This effect has been demonstrated by a competitive reaction between two ketones, which is indicated by the following reactions (Scheme 2). This is also a general trend for the reduction of ketones with this reagent (Table 2). [Zn(BH$_4$)$_2$(dabco)] is advantageous over our previously reported reagent, cross-linked poly(4-vinylpyridine)-supported zinc tetrahydroborate [XP4-Zn(BH$_4$)$_2$],[50)] which is very sluggish for the reduction of ketones. In order to show both the advantages and limitations of the reagent, we compared our results with those reported with [XP4-Zn(BH$_4$)$_2$],[50)] Zn(BH$_4$)$_2$,[48)] 1-benzyl-4-aza-1-azoniabicyclo[2.2.2]octane tetrahydroborate (BAAOTB),[44a)] and tetrabutylammonium tetrahydroborate (TBATB)[44b)] (Table 4).

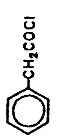
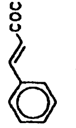
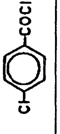
2. Reduction of α-Diketones, and Acyloins. The reduction of α-diketones to their diols usually gives a mixture of the diol and the corresponding acyloin. With this reagent α-diketones are reduced very easily to their corresponding vicinal diols with excellent yields (Table 5). Attempts to reduce α-diketones to their corresponding acyloins have been unsatisfactory, and only the corresponding vicinal diols have been isolated from a mixture with high yields.

Acyloins are also reduced very easily to their vicinal diols in excellent yields with this reagent (Table 5).

3. Reduction of α,β-Unsaturated Aldehydes and Ketones. Allyl alcohols are important synthetic precursors. A regioselective reduction of α,β-unsaturated aldehydes and ketones is an easy way to obtain these compounds. Therefore, this achievement is synthetically very important.[1,4,56,57)] The reduction of α,β-unsaturated carbonyl compounds with NaBH$_4$ is highly solvent dependent and generally does not result in a useful regioselectivity.[9,58)]

The selective reduction of these systems has stimulated considerable interest, leading to the development of new reagents for selective 1,4-[15,59)] and 1,2-reductions[9,21,23,31,60)] of α,β-unsaturated aldehydes and ketones. Selective 1,2-reduction is usually achieved using modified hydride reagents, which are formed by the replacement of hydride with ster-

Table 9. Comparison of Reduction of Acyl Chlorides to the Alcohols with $[Zn(BH_4)_2(dabco)]$, $[XP4\text{-}Zn(BH_4)_2]$,[a] $Zn(BH_4)_2/TMEDA$,[b] $[Zn(BH_4)_2(pyz)]_n$,[c] BAAOTB,[d] and TBATB[e]

Entry	Substrate	$[Zn(BH_4)_2(dabco)]$		$[XP4\text{-}Zn(BH_4)_2]$[64]			$Zn(BH_4)_2/TMEDA$[49a,b]		$[Zn(BH_4)_2(pyz)]_n$[52a]		BAAOTB[45]		TBATB[45]	
		Molar ratio	Yield (%) (h)	Molar ratio	Yield (%) (h) alcohol	Yield (%) aldehyde	Molar ratio	Yield (%) (h)	Molar ratio	Yield (%) (h)	Molar ratio	Yield (%) (h)	Molar ratio	Yield (%) (h)
1		3	91 (0.5)	2	70 (20)	20	1.4	98 (0.5)	2	95 (3)	3	85 (2)	1	85 (1.5)
2		3	88 (20)	2	70 (10)	15	1.4	93 (0.25)	2	98 (6)	3	95 (2)	1	85 (1)
3		3	92 (2.5)	—	—	—	—	—	—	—	3	85 (2.5)	1	95 (1)
4		3	91 (0.8)	2	85 (12)	5	1.4	86 (0.5)	—	—	3	80 (3)	1	85 (1)
5		3	88 (3.7)	2	50 (24)	35	1.4	89 (0.5)	—	—	—	—	—	—
6		3	93 (2.5)	2	60 (18)	30	1.4	—	—	—	—	—	—	—

a) Cross-linked poly(4-vinylpyridine) supported zinc tetrahydroborate. b) Zinc teterahydroborate and *N*,*N*, *N'*, *N'*-tetramethylethylenediamine. c) Poly[tetrahydro[(1,4-*η*)pyrazine]boratozinc]. d) 1-Benzyl-4-aza-1-azoniabicyclo[2.2.2]octane tetrahydroborate. e) Tetrabutylammonium tetrahydroborate.

ically bulky substituents or electron-withdrawing groups in order to discriminate between the structural or electron environments of the carbonyl groups.[1,4,9,21,23,59,60]

Whereas the reduction of aldehydes is achieved by $[Zn(BH_4)_2(dabco)]$ in THF at room temperature, the reduction of ketones requires a higher temperature, and should be performed in refluxing THF. The chemo and regioselectivity of the reagent is demonstrated by the following competitive reaction (Scheme 3) and (Table 2). The selectivity ratio for the 1,2-reduction of the aldehyde with respect to the ketone is 32. The polymeric analogue of the reagent, cross-linked poly(4-vinylpyridine)-supported zinc tetrahydroborate $[XP4\text{-}Zn(BH_4)_2]$, even in refluxing EtOH, is not able to transform the α,β-unsaturated ketones to alcohols (Table 6).

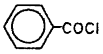
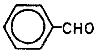
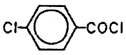
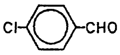
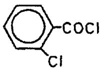
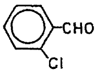
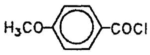
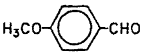
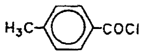
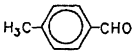
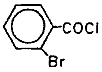
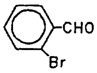
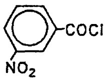
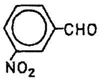
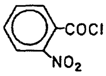
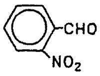
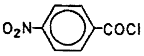
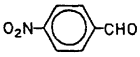
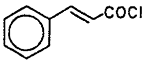
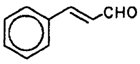
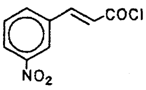
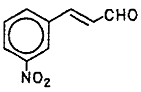
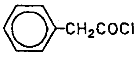
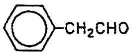
We have compared our results with those obtained by $[XP4\text{-}Zn(BH_4)_2]$, $Zn(BH_4)_2$, 1-benzyl-4-aza-1-azoniabicyclo[2.2.2]octane tetrahydroborate (BAAOTB), and tetrabutylammonium tetrahydroborate (TBATB), as are shown in Table 7. A comparison of the results shows that this reagent is more efficient than those mentioned above.

4. Reduction of Acyl Chlorides. Primary studies concerning the reduction of acyl chlorides with $NaBH_4$ involve vigorous conditions, and only alcohols have been obtained.[61] However, this method is less effective for polyfunctional and conjugated acyl chlorides, and produce different products.[61,62] In order to surmount this disadvantage, several modified procedures have been introduced in the literature.[44b,49a,49b,63] $Zn(BH_4)_2$ in the presence of *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (TMEDA) is reported to be a remarkably mild method for the reduction of acyl chlorides to the corresponding alcohols at 0—40 °C.[49a,49b]

We have studied the reduction of a series of acyl chlorides with $[Zn(BH_4)_2(dabco)]$ in THF at room temperature. The reaction performs very well in 0.08—3.4 h, and produces the corresponding alcohols in high yields (85—93%). 4-Nitrobenzoyl chloride is an exception, and the reduction proceeds with a longer reaction time (20 h). $[Zn(BH_4)_2(dabco)]$ in THF is a highly chemoselective reagent for the 1,2-reduction of α,β-unsaturated acyl chlorides to their corresponding allyl alcohols (Table 8). Aldehydes are not detected in the reaction mixture. We have compared the results of our experiments with some of those reported with cross-linked poly(4-vinylpyridine)-supported zinc tetrahydroborate: $[XP4\text{-}Zn(BH_4)_2]$,[64] poly[tetrahydro[(1,4-*η*)pyrazine]boratozinc] ; $[Zn(BH_4)_2(pyz)]_n$,[52a] $Zn(BH_4)_2/TMEDA$,[49a,49b] $(Bu)_4NBH$; (TBATB),[45] and 1-benzyl-4-aza-1-azoniabicyclo[2.2.2]octane tetrahydroborate (BAAOTB) a very recently reported reagent.[44a,45] $[XP4\text{-}Zn(BH_4)_2]$ as a modified borohydride reagent is not able to produce alcohols from acyl chlorides as the sole product, and the reaction mixture is always contaminated with appreciable amounts of aldehydes (Table 9).

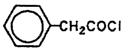
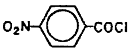
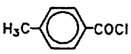
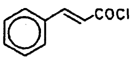
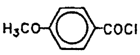
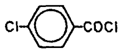
The conversion of acyl chlorides to their corresponding aldehydes is an important transformation in organic synthesis. Methods, such as catalytic hydrogenation (Rosenmund reduction)[65] and lithium tri(*t*-butoxy)aluminum hydride,[66] have been used for a long time with difficulty. Amberlyst

Table 10. Reduction of Acyl Chlorides to Aldehydes with [$Zn(BH_4)_2$(dabco)][a]

Entry	Substrate	Product	Red/Subs	Time (h)	Conversion (%)	Yield (%)	Mp or bp (°C)[69]
1			1.5	3.5	100	90	178—179
2			1.5	2.4	100	90	47—50
3			1.5	0.16	100	89	209—215
4			1.5	6.4	100	86	248
5			1.5	4.5	100	89	205—207
6			1.5	0.16	100	87	230
7			1.5	0.25	100	90	57—59
8			1.5	0.13	100	90	43—46
9			1.5	48	0	—	105—108
10			1.5	0.25	100	89	248
11			1.5	0.16	100	90	—
12			1.5	1.8	100	85	195

a) All reactions were performed in CH_2Cl_2 : hexane / 7 : 1 at room temperature.

Table 11. Comparison of Reduction of Acyl Chlorides to the Aldehydes with [$Zn(BH_4)_2$(dabco)], [XP4-$Zn(BH_4)_2$],[a] BAAOTB[b]

Entry	Substrate	[$Zn(BH_4)_2$(dabco)]			[XP4-$Zn(BH_4)_2$][54]			BAAOTB[45]	
		Molar ratio	Yield (%) (h) alcohol	Yield (%) aldehyde	Molar ratio	Yield (%) (h) alcohol	Yield (%) aldehyde	Molar ratio	Yield (%) (h) aldehyde
1		1.5	<7 (1.8)	85	2	25 (7)	65	2	70 (1)
2		2	0 (24)	0	2	10 (5)	87	2	75 (1.5)
3		1.5	<7 (4.5)	89	—	—	—	2	95 (10)
4		1.5	<7 (0.25)	89	2	20 (7)	70	2	60 (4)
5		1.5	<7 (6.4)	86	2	30 (18)	60	—	—
6		1.5	<7 (2.4)	90	2	15 (12)	75	—	—

a) Cross-linked poly(4-vinylpyridine) supported zinc tetrahydroborate. b) 1-Benzyl-4-aza-1-azoniabicyclo[2.2.2]octane tetrahydroborate.

A-26 supported borohydride,[67] $[Cu(BH_4)(Ph_3P)_2]$,[38,41] and $[Cu_2(BH_3CN)_2(Ph_3P)_4]$[40] under controlled conditions have also been used for this purpose. In recent years, several other reducing agents have also been developed for this purpose.[68]

We have studied the possibility of reducing acyl chlorides to aldehydes with $[Zn(BH_4)_2(dabco)]$. We have found that the behavior and the reducing ability of this reagent is very solvent dependent, and in a mixture of CH_2Cl_2/hexane (7 : 1) is able to transform acyl chlorides to their corresponding aldehydes with high chemoselectivity (Table 10). This conversion usually takes place easily (0.13—4.3 h) with high yields (87—92%). α,β-Unsaturated acyl chlorides produce their aldehydes without affecting their C–C double bonds. 4-Nitrobenzoyl chloride remains intact, and even after 48 h the starting material can be isolated from the mixture. The alcohol contamination in the reaction mixtures, under our studies, is less than 7%. We have compared our results with some of those reported concerning $[XP4\text{-}Zn(BH_4)_2]$[66] and BAAOTB[45] in (Table 11).

$[Zn(BH_4)_2(dabco)]$ shows a different behavior than its analogue cross-linked poly(4-vinylpyridine)-supported zinc tetrahydroborate $[XP4\text{-}Zn(BH_4)_2]$ and a mixture of $Zn(BH_4)_2$/TMEDA, but is very similar to BAAOTB, which also has the dabco moiety in its structure. This observation reflects the importance of the structural effect upon the chemical and physical properties of the compounds, e.g. stability, selectivity, solubility behavior, and reduction ability.

Conclusion

In this article we have shown that dabco is a good ligand for stabilizing $Zn(BH_4)_2$, and does not also affect the reducing ability of the reagent. Comparatively, the rate of the reactions is usually, more or less, the same as those reported for $Zn(BH_4)_2$. The stability, high yields of the products, ease of preparation from commercially available materials, high chemoselectivity of the reagent, and also easy work-up of the mixture makes this new modified borohydride compound an attractive practical bench-top reagent and a synthetically useful addition to transition-metal tetrahydroborate complexes.

Experimental

General: Yields refer to isolated products. Reactions proceeded in THF. The products were characterized by a comparison with authentic samples (IR, ^1H NMR, GLC, and TLC)

Preparation of (1,4-Diazabicyclo[2.2.2]octane)(tetrahydroborato)zinc $[Zn(BH_4)_2(dabco)]$. An ethereal solution of $Zn(BH_4)_2$ (0.16 M, 500 ml, 1 M = 1 mol dm^{-3}) was prepared according to an available procedure in the literature;[25] then dabco (8.97 g, 0.08 mol) in ether (200 ml) was added dropwise to a $Zn(BH_4)_2$ solution and stirred for 2 h. The resulting precipitate was filtered and washed with ether (100 ml), and dried in a vacuum to afford a white solid (15.5 g, 97% yield), which was decomposed at 255 °C to a dark-grayish material.

A Typical Procedure for the Reduction of Aldehyde to Alcohol with $[Zn(BH_4)_2(dabco)]$. In a round-bottomed flask (25 ml), equipped with a magnetic stirrer, a solution of 4-chlorobenzaldehyde (0.14 g, 1 mmol) in THF (8 ml) was prepared. The reducing agent (0.166 g, 0.75 mmol) was added and the resulting mixture was stirred magnetically at room temperature for 0.5 h. The progress of the reaction was monitored by TLC (eluent; CCl_4/Et_2O: 5/1). After completion of the reaction, methanol (2 ml) was added to the reaction mixture and was magnetically stirred for 2h. The solvent was then evaporated and the resulting crude material was purified by silica-gel column chromatography using CCl_4/Et_2O: 5/2 as the eluent. Evaporation of the solvent afforded pure crystals of 4-chlorobenzyl alcohol (0.13 g, 92% yield, Table 1).

A Typical Procedure for the Reduction of Ketone to Alcohol with $[Zn(BH_4)_2(dabco)]$. In a round-bottomed flask (25 ml) equipped with a magnetic stirrer and a condenser, a solution of benzophenone (0.182 g, 1 mmol) in THF (8 ml) was prepared. A reducing agent (0.31g, 1.5 mmol) was added and the reaction mixture was magnetically stirred under reflux conditions for 8.3 h. The progress of the reaction was monitored by TLC (eluent; CCl_4/Et_2O: 5/1). After completion of the reaction, methanol (2 ml) was added to the mixture and was magnetically stirred for 2 h. The solvent was evaporated and the resulting crude material was purified by silica-gel column chromatography using CCl_4/Et_2O: 5/2 as the eluent. Evaporation of the solvent afforded pure crystals of diphenylmethanol (0.173 g, 94% yield, Table 3).

A Typical Procedure for Selective 1,2-Reduction of α,β-Unsaturated Aldehydes with $[Zn(BH_4)_2(dabco)]$. In a round-bottomed flask (25 ml) equipped with a magnetic stirrer a solution of cinnamaldehyde (0.13 g, 1 mmol) in THF (10 ml) was prepared. The reducing agent (0.155 g, 0.75 mmol) was added and the resulting mixture was stirred magnetically at room temperature for 4.3 h. The progress of the reaction was monitored by TLC (eluent; CCl_4/Et_2O: 5/2) or GLC. After completion of the reaction, methanol (2 ml) was added to the mixture, and was magnetically stirred for 2 h. The solvent was evaporated and the resulting crude material was purified by silica-gel column chromatography using CCl_4/Et_2O: 5/3 as the eluent. After evaporation of the solvent pure cinnamyl alcohol was obtained (0.125 g, 94% yield, Table 6).

A Typical Procedure for Selective 1,2-Reduction of α,β-Unsaturated Ketones with $[Zn(BH_4)_2(dabco)]$. In a round-bottomed flask (25 ml) equipped with a magnetic stirrer and a condenser a solution of benzylideneacetone (0.146 g, 1 mmol) in THF (10 ml) was prepared. The reducing agent (0.25 g, 1.2 mmol) was added to the solution, and the resulting reaction mixture was stirred magnetically under reflux conditions for 2 h. The progress of the reaction was monitored by TLC (eluent; CCl_4/Et_2O: 5/2) or GLC. After completion of the reaction, methanol (2 ml) was added to the mixture, and was magnetically stirred for 2 h. The solvent was evaporated and the resulting crude material was purified by silica-gel column chromatography using CCl_4/Et_2O: 5/3 as the eluent. After evaporation of the solvent pure 4-phenyl-3-buten-2-ol was obtained (0.136 g, 92% yield, Table 6).

A Typical Procedure for the Reduction of Acyl Chlorides to Alcohols with $[Zn(BH_4)_2(dabco)]$. In a round-bottomed flask (25 ml), equipped with a magnetic stirrer, a solution of 3-nitrobenzoyl chloride (0.185 g, 1 mmol) in THF (8 ml) was prepared. The reducing agent (0.63 g, 3 mmol) was added to the solution and the resulting mixture was magnetically stirred at room temperature for 5 min. The progress of the reaction was monitored by TLC (eluent; CCl_4/Et_2O: 5/2). After completion of the reaction, methanol (2 ml) was added to the reaction mixture, and it was magnetically stirred for 2 h. The solvent was evaporated and the resulting crude material was purified by silica-gel column chromatography (eluent; CCl_4/Et_2O: 5/3). Pure 3-nitrobenzyl alcohol was obtained (0.137 g, 90% yield, Table 8).

A Typical Procedure for the Reduction of Acyl Chlorides to

Aldehydes with [Zn(BH$_4$)$_2$(dabco)]. In a round-bottomed flask (25 ml) equipped with a magnetic stirrer a solution of 3-nitrobenzoyl chloride (0.18 g, 1 mmol) in a mixture of CH$_2$Cl$_2$/hexane: 7/1 (8 ml) was prepared. The reducing agent (0.3 g, 1.5 mmol) was added to the solution and the resulting mixture was magnetically stirred at room temperature for 15 min. The progress of the reaction was monitored by TLC (eluent; CCl$_4$/Et$_2$O: 6/1). After completion of the reaction, the solvent was evaporated and the resulting crude material was purified by silica-gel column chromatography (eluent; CCl$_4$/Et$_2$O: 6/2). Pure 3-nitrobenzaldehyde was obtained (0.136 g, 90% yield, Table 10).

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