Selective Reduction of Carbonyl Compounds with *Al*-Alkoxydiisobutylalanes

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Reaction of carbonyl compounds with *Al*-alkoxydiisobutylalane (DIBAOR, R=H, Et, *i*-Pr, *t*-Bu) has been investigated in detail so as to establish their usefulness as selective reducing agents in organic synthesis. The reagents appear to be extremely mild and can reduce only aldehydes and ketones effectively under mild conditions. All the other common organic functional groups are not affected by these reagents. The reagents can also reduce α,β-unsaturated aldehydes and ketones to the corresponding allylic alcohols without any detectable 1,4-reduction. Furthermore, the reagents show a highly chemoselective discrimination between aldehyde and ketone, between aldehydes, and between ketones. Even more remarkable is the stereoselective reduction of cyclic ketones to the thermodynamically more stable alcohol epimers.

Introduction

Recently, we reported that *Al*-chlorodiisobutylalane (DIBACl) is an extremely efficient chemoselective reducing agent for the reduction of α,β-unsaturated carbonyl compounds to allylic alcohols[1] and for the competitive reduction between carbonyl compounds.[2] Such a high chemoselectivity seems to appear due to the result from the selective coordination of the aluminum atom of reagent to the carbonyl oxygen of compounds followed by the hydride transfer to the carbonyl carbon through dehydroalumination *via* a cyclic boatlike transition state, as in the case of *B*-halodiisopinocampheylboranes.[3] These fascinating results prompted us to examine the alkoxy substituted derivatives of diisobutylalane, *Al*-alkoxydiisobutylalanes (DIBAOR). We prepared a series of DIBAOR (R=H, Et, *i*-Pr, *t*-Bu), examined their reactivities toward general organic functional groups, and finally investigated their selectivities in the reduction of aldehydes and ketones.

A portion of our results has appeared in the form of preliminary communications.[4] We now describe in full the result of our study on the reduction characteristics of *Al*-alkoxydiisobutylalanes.

Results and Discussion

DIBAOH was prepared by treatment of diisobutylaluminum hydride (DIBAH) in ethyl ether (EE) with 1 equivalent of water (Eq. 1). The other DIBAOR was made by a simple reaction between DIBAH and the corresponding alcohols in EE (Eq. 2). The ^{27}Al NMR spectra of DIBAOR in EE revealed a broad singlet at δ 72 ppm for **1**, δ 152 for **2**, δ 160 for **3** and δ 164 for **4**, relative to $[Al(H_2O)_6]^{3+}$.

$$i\text{-Bu}_2\text{AlH} + \text{H}_2\text{O} \xrightarrow[\text{RT}]{\text{Et}_2\text{O}} i\text{-Bu}_2\text{AlOH} + \text{H}_2\uparrow \quad (1)$$
DIBAOH, **1**

$$i\text{-Bu}_2\text{AlH} + \text{ROH} \xrightarrow[0\ ^\circ\text{C}]{\text{Et}_2\text{O}} i\text{-Bu}_2\text{AlOR} + \text{H}_2\uparrow \quad (2)$$

R=Et, DIBAOEt, **2**
i-Pr, DIBAO^{i}Pr, **3**
t-Bu, DIBAO^{t}Bu, **4**

Reactivities toward aldehydes, ketones and other reducible compounds. The reactivities of DIBAOR toward some representative aldehydes, ketones and other reducible compounds were examined, and the results are presented in Table 1. In general, all the alkoxy derivatives examined appear to be much milder than DIBACl.[1,2] The relative reactivity of DIBAOR is in the order of DIBAOH> DIBAOEt>DIBAO^{i}Pr>DIBAO^{t}Bu. Apparently, such a reactivity order arises from the size of the alkoxy substituent. Aldehydes were reduced readily to the corresponding alcohols, while the complete reduction of ketones required a prolonged reaction time (1 or 3 days) under these reaction conditions. However, other general functional groups, such as esters, nitriles and even acid chlorides, the most susceptible functional groups, were absolutely inert to these reagents. Such a striking feature observed in this experiment led us to investigate their chemoselectivities in the reduction of aldehydes and ketones in detail.

Selective reduction of α,β-unsaturated aldehydes and ketones. Selective 1,2-reduction of α,β-unsaturated aldehydes and ketones with metal complex hydride reducing agents is often difficult due to competing 1,2- *vs.* 1,4-attack by hydride.[5] Among the various reducing systems which have been developed for such purpose, some metal hydride systems have proven to be efficient and convenient.[6,7]

The reductions of enals and enones were carried out by the addition of two equivalents of DIBAOR to the carbonyl compounds in EE at 25 °C and the products were analyzed by GC (Table 2). Reduction of simple conjugated aldehydes, such as crotonaldehyde, 2-hexenal and cinnamaldehyde, afforded entirely the corresponding allylic alcohols, resulting only from 1,2-reduction. In the case of acyclic enones, such as 3-penten-2-one, benzalacetone and chalcone, the reaction also proceeded cleanly in a 1,2-sense to give the corresponding allylic alcohols in essentially quantitative yields

Table 1. Reduction of representative aldehydes, ketones and other functional compounds with *Al*-alkoxydiisobutylalane (DIBAOR) in ethyl ether at 25 ℃[a]

Compound	Reagent[b]	Time (hr)	Reduction (%)[c]
Hexanal	**1**	3	100
	2	3	99.9
		6	100
	3	3	99
		6	100
	4	6	99
		12	100
Benzaldehyde	**1**	1	99.9
		3	100
	2	1	99.9
		3	100
	3	1	98
		3	100
	4	3	98
		6	100
2-Butanone	**1**	24	100
	2	48	>99.9
	3	48	99.9
	4	48	90
		72	100
Acetophenone	**1**	12	100
	2	48	100
	3	48	>99.9
	4	48	90
		72	100
Norcamphor	**1**	24	85[d]
	3	24	76[e]
Hexanoyl chloride	**1**	24	0
	2	24	0
	3	24	0
	4	24	0
Ethyl caproate	**1**	24	0
	2	24	0
	3	24	0
	4	24	0
Benzonitrile	**1**	24	0
	2	24	0
	3	24	0
	4	24	0

[a]Ten % excess reagent was utilized. [b]DIBAOH, **1**; DIBAOEt, **2**; DIBAO^{i}Pr, **3**; DIBAO^{t}Bu, **4**. [c]GC yields with suitable internal standard. [d]Eighty % *exo*-norborneol. [e]Ninety % *exo*-norborneol.

at 25 ℃. 2-Cyclohexenone was readily reduced to 2-cyclohexenol in a quantitative yield. Even 2-cyclopentenone,

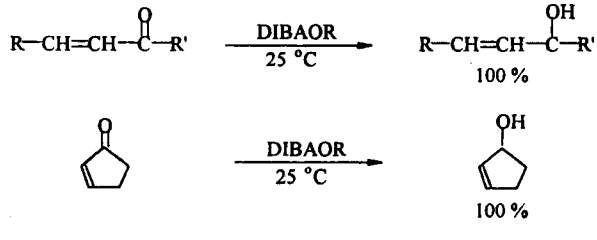


Table 2. Reduction of α,β-unsaturated aldehydes and ketones with DIBAOR in ethyl ether at 25 ℃[a]

Compound	Reagent[b]	Time (hr)	Product ratio[c] (1,2 : 1,4)	Yield (%)[c]
Crotonaldehyde	**1**	3	100 : 0	>99.9
	2	3	100 : 0	97
		6	100 : 0	100 (78)
	3	3	100 : 0	95
		6	100 : 0	99
		12	100 : 0	100
	4	3	100 : 0	84
		6	100 : 0	90
		12	100 : 0	95
		24	100 : 0	100
2-Hexenal	**1**	6	100 : 0	100
	2	6	100 : 0	94
		12	100 : 0	98
		24	100 : 0	100 (76)
	3	6	100 : 0	90
		12	100 : 0	97
		24	100 : 0	100
	4	6	100 : 0	85
		12	100 : 0	89
		24	100 : 0	95
		72	100 : 0	100
Cinnamaldehyde	**1**	6	100 : 0	100
	2	6	100 : 0	99
		12	100 : 0	100
	3	6	100 : 0	99
		12	100 : 0	100
	4	6	100 : 0	93
		12	100 : 0	97
		24	100 : 0	99
		48	100 : 0	100
3-Penten-2-one	**1**	6	100 : 0	100
	2	6	100 : 0	98
		24	100 : 0	100
	3	6	100 : 0	96
		24	100 : 0	100
	4	6	100 : 0	93
		24	100 : 0	97
		72	100 : 0	100
Benzalacetone	**1**	24	100 : 0	98
		72	100 : 0	100
	2	24	100 : 0	84
		72	100 : 0	100
	3	24	100 : 0	86
		72	100 : 0	94
		120	100 : 0	100
	4	24	100 : 0	60
		72	100 : 0	72
		120	100 : 0	87
		240	100 : 0	100
Chalcone	**1**	72	100 : 0	86
		120	100 : 0	100
	2	72	100 : 0	78
		120	100 : 0	91
		240	100 : 0	100
	3	72	100 : 0	65
		120	100 : 0	84

Table 2. Continued

Compound	Reagent[b]	Time (hr)	Product ratio[c] (1,2 : 1,4)	Yield (%)[c]
		168	100 : 0	90
		240	100 : 0	>99.9
	4	72	100 : 0	43
		120	100 : 0	64
		168	100 : 0	77
		240	100 : 0	86, 100[d]
2-Cyclopenten-1-one	**1**	24	100 : 0	100
	2	24	100 : 0	96
		72	100 : 0	100 (80)
	3	24	100 : 0	89
		72	100 : 0	96
		120	100 : 0	100
	4	24	100 : 0	74
		72	100 : 0	82
		120	100 : 0	91
		240	100 : 0	100
2-Cyclohexen-1-one	**1**	24	100 : 0	100
	2	24	100 : 0	>99.9
	3	24	100 : 0	92
		72	100 : 0	100
	4	24	100 : 0	87
		72	100 : 0	96
		120	100 : 0	>99.9
Isophorone	**1**	72	100 : 0	100
	2	72	100 : 0	100
	3	72	100 : 0	93
		120	100 : 0	>99.9
	4	72	100 : 0	69
		120	100 : 0	84
		240	100 : 0	100

[a]Two equivalents of reagent were utilized. Reaction mixtures were *ca.* 1 M in substrates. [b]DIBAOH, **1**; DIBAOEt, **2**; DIBAO^{i}Pr, **3**; DIBAO^{t}Bu, **4**. [c]Determined by GC using suitable internal standard. Numbers in parentheses indicate isolated yields.

known for its susceptibility to undergo conjugate reduction, was cleanly converted to the desired 2-cyclopentenol in a quantitative yield. Similarly, isophorone was also readily reduced to 3,3,5-trimethyl-2-cyclohexen-1-ol.

The results summarized in Table 2 cleanly reveal that the reagents are ideal for the selective reduction of α,β-unsaturated aldehydes and ketones to the corresponding allylic alcohols, even though some hindered ketones require longer reaction time for completion. The selectivity reaches 100%. Furthermore, DIBAOR is extremely mild: various functional groups are compatible. In addition, by appropriate introduction of alkoxy groups to DIBAH it should be possible to adjust the reducing power of the reagents whenever necessary.

Like the case of DIBACl, such a perfect selectivity seems to arise from the cyclic mechanism in which the β-hydride of the isobutyl group is shifted to the carbonyl carbon of the substrate.[1,2]

Ipc_2BOR also appears to be a reagent of choice in the 1,2-reduction of α,β-unsaturated aldehydes.[8] However, α,β-unsaturated ketones are absolutely inert to Ipc_2BOR.[9] This provides another advantage to this reagent: Ipc_2BOR achieves the selective 1,2-reduction of α,β-unsaturated aldehydes in the presence of α,β-unsaturated ketones.[8]

Selective reduction of aldehydes or keto group in the presence of aldehyde, keto or other functional groups. The chemoselective reduction between structurally different carbonyl compounds affords a very useful methodology in organic synthesis. Consequently, in recent years, numerous reagents have been proposed to achieve such objective.[10] However, a really ideal reagent had escaped us. Very recently, we reported that Ipc_2BX,[3b,c] Ipc_2BOR[8,9] and DIBACl[2] are extremely efficient chemoselective reducing agents for such purpose.

The chemoselectivity of DIBAOR was tested with twenty-four representative pairs in competition experiments. Equimolar amounts of two compounds were allowed to compete for a limited quantity of DIBAOR. After appropriate time intervals, the mixture was hydrolyzed and the results obtained by GC analysis are summarized in Table 3.

As mentioned above, the relative reactivity of DIBAOR is in the order of DIBAOH>DIBAOEt≥DIBAO^{i}Pr>DIBAO^{t}Bu. On the contrary, the relative selectivity in the competitive reaction appears to be in the reverse order. In general, all the reagents, except DIBAOH, are highly selective toward aldehydes and ketones. DIBAOH shows less selectivity than the other reagents.

Both aliphatic and aromatic aldehydes examined were selectively reduced in the presence of quite a number of different ketones (Entries 9-11): a wide variety of aldehydes were selectively reduced in the presence of a more reactive ketone, cyclohexanone (Entries 7, 8 and 12). Even more remarkable is the chemoselective discrimination between aldehydes. Thus, benzaldehyde can be selectively reduced in the presence of hexanal (Entries 2 and 14) or *p*-anisaldehyde (Entry 6). Butanal and hexanal are much more reactive than *p*-anisaldehyde toward the reagents (Entries 3 and 5). Futhermore, the reagent can discriminate between structurally different ketones (Entries 13-19). Even cyclohexanone can be selectively reduced in the presence of cyclopentanone in a 95 : 5 selectivity with DIBAO^{t}Bu (Entry 13). In addition, various functional groups, such as esters, nitriles, amides and alkenes, are not affected by DI-

BAOR. Even acid chlorides are inert to the reagents.

Such a remarkable inertness toward most of the reducible functional groups, combined with a high selectivity for the reduction of aldehydes and ketones, has already been realized with DIBACl[2]. However, the reducing power of DIBAOR is much weaker than that of DIBACl and, hence, seems to be more applicable for such chemoselective reductions in complex molecules.

Stereoselective reduction of cyclic ketones with DIBAO^{i}Pr. In recent years, new developments in the area of stereoselective reduction of cyclic ketones have been exceptionally encouraging. Especially, the reagents de-

Table 3. Chemoselective reduction of carbonyl compounds with DIBAOR in ethyl ether at 25 ℃[a]

Entry	Starting mixture	Reagent[b]	Time (hr)	Ratio of redn products[c]
1	Butanal/Hexanal	**1**	3	57 : 43
		2	6	60 : 40
		3	6	65 : 35
		4	12	66 : 34
2	Butanal/Benzaldehyde	**1**	3	20 : 80
		2	6	5 : 95
		3	6	4 : 96
		4	12	3 : 97
3	Butanal/*p*-Anisaldehyde	**1**	3	86 : 14
		2	6	95 : 5
		3	6	96 : 4
		4	12	99 : 1
4	Hexanal/Benzaldehyde	**1**	3	20 : 80
		2	3	2 : 98
		3	3	1 : 99
		4	6	0.5 : 99.5
5	Hexanal/*p*-Anisaldehyde	**1**	3	83 : 17
		2	6	92 : 8
		3	6	93 : 7
		4	12	99 : 1
6	Benzaldehyde/*p*-Anisaldehyde	**1**	3	90 : 10
		2	3	99.5 : 0.5
		3	3	99.5 : 0.5
		4	6	>99.9 : tr
7	Butanal/Cyclohexanone	**1**	3	81 : 19
		2	6	100 : 0
		3	6	99.9 : 0.1
		4	12	100 : 0
8	Hexanal/Cyclohexanone	**1**	3	85 : 15
		2	6	100 : 0
		3	6	98 : 2
		4	12	>99.9 : tr
9	Hexanal/2-Heptanone	**1**	3	91 : 9
		2	6	100 : 0
		3	6	100 : 0
		4	12	100 : 0
10	Hexanal/Acetophenone	**1**	3	90 : 10
		2	6	100 : 0
		3	6	99 : 1
		4	12	99.5 : 0.5
11	Hexanal/Benzophenone	**1**	3	95 : 5
		2	6	100 : 0
		3	6	100 : 0
		4	12	100 : 0
12	*p*-Anisaldehyde/Cyclohexanone	**1**	3	80 : 20
		2	12	99 : 1
		3	12	90 : 10
		4	12	95 : 5
13	Cyclohexanone/Cyclopentanone	**1**	24	55 : 45
		2	24	90 : 10
		3	24	92 : 8
		4	48	95 : 5
14	Cyclohexanone/2-Heptanone	**1**	24	60 : 40
		2	24	100 : 0
		3	24	100 : 0
		4	48	100 : 0
15	Cyclohexanone/Acetophenone	**1**	24	67 : 33
		2	24	95 : 5
		3	24	90 : 10
		4	48	90 : 10
16	Cyclohexanone/Benzophenone	**1**	24	76 : 24
		2	24	100 : 0
		3	24	100 : 0
		4	48	100 : 0
17	Acetophenone/2-Heptanone	**1**	48	55 : 45
		2	48	100 : 0
		3	48	>99.9 : tr
		4	72	96 : 4
18	2-Heptanone/Benzophenone	**1**	96	53 : 47
		2	96	95 : 5
		3	96	94 : 6
		4	120	94 : 6
19	Acetophenone/Benzophenone	**1**	48	57 : 43
		2	48	100 : 0
		3	48	100 : 0
		4	72	96 : 4
20	Hexanal/Hexanoyl chloride	**1**	3	100 : 0
		2	6	100 : 0
		3	6	100 : 0
		4	12	100 : 0
21	Hexanal/Benzoyl chloride	**1**	3	100 : 0
		2	6	100 : 0
		3	6	100 : 0
		4	12	100 : 0
22	2-Heptanone/Benzoyl chloride	**1**	24	98 : 2
		2	96	99 : 1
		3	96	100 : 0
		4	120	100 : 0
23	Hexanal/Hexanenitrile	**1**	6	100 : 0
		2	6	100 : 0
		3	6	100 : 0
		4	12	100 : 0
24	Hexanal/Ethyl hexanoate	***1***	6	100 : 0
		2	6	100 : 0
		3	6	100 : 0
		4	12	100 : 0

[a]Reaction mixtures were *ca.* 1 M in substrates. One equivalent of reagent was utilized for competitive reduction of equimolar mixture of two carbonyl compounds. [b]DIBAOH, **1**; DIBAOEt, **2**; DIBAO^{i}Pr, **3**; DIBAO^{t}Bu, **4**. [c]Normalized ratio determined by GC using appropriate internal standard; the total yields of product alcohols were ≥99%.

veloped for conversion of cyclic ketones to the thermodynamically less stable alcohols are extraordinary.[11] However, although several useful reagents have been devised for converting cyclic ketones to the thermodynamically more stable alcohols,[12] generally acceptable synthetic methods for this conversion have still been lacking.

Initially, we examined only the reaction in which an equimolar mixture of DIBAO^{i}Pr and ketone is involved at 25 ℃. However, we soon realized that, like triisobutylaluminum (TIBA),[13] the isobutyl group of DI-

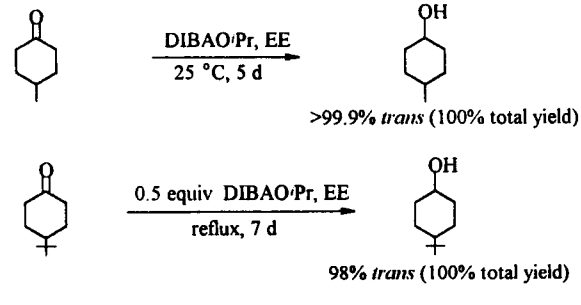
Table 4. Stereoselective reduction of cyclic ketones with DIBAOR in ethyl ether

Ketone	Reagent	Rgt/ compd	Temp. (℃)	Reaction time (d)	Ratio of more stable isomer (%)[a]	Yield of alcohol (%)[a]
2-Methylcyclohexanone						
	1	2	25	1	86	74
	3	1	25	0.25	67	71
				1	85	92
				3	91	98
				4	94	99
				5	95	>99.9
				7	96	100(82)
		0.5	reflux	1	87	76
				3	89.5	87
				7	92	93
				10	93	96
				15	93.5	99
				20	93.5	100
3-Methylcyclohexanone						
	1	2	25	1	91	95
	3	1	25	0.25	91	98
				1	93	99
				3	93	>99.9
				4	94	100
				5	95	100
		0.5	reflux	1	91	81
				3	92	92
				7	93	98
				10	94	>99.9
				15	95	100
4-Methylcyclohexanone						
	1	2	25	1	88	98
	3	1	25	1	92	99
				3	94	>99.9
				4	97	100
				5	>99.9	100
		0.5	reflux	1	92	87
				3	93.5	94
				7	95	98
				10	97	100
4-t-Butylcyclohexanone						
	1	2	25	1	96	80
	3	1	25	0.25	91	98
				1	95	>99.9
				2	95	100
				3	97	100
				4	98	100(84)
		0.5	reflux	1	91	82
				3	94.5	94
				5	97	97
				7	98	>99.9
				10	98	100
3,3,5-Trimethylcyclohexanone						
	1	2	25	1	97	67
	3	1	25	0.5	97	89
				1	98	94
				3	>99.9	99
				4	>99.9	100
		0.5	reflux	1	93	78.5
				3	94	89
				7	96	97
				10	98	100
Norcamphor	**1**	2	25	1	80	85
	3	1	25	0.25	85	43
				1	90	76
				3	93	96
				4	95	>99.9
				5	97	100
		0.5	reflux	1	68	58
				3	81	73
				7	89	95
				10	91.5	98
				15	92	100
Camphor	**1**	2	25	1	46	87
	3	1	25	1	31	7
				5	36	14
				7	37	23
		0.5	reflux	1	35	2.5
				3	37	5
				7	42.5	6.5
				10	56	10.5
				15	69	20

[a]Analyzed by GC. The numbers in parentheses are isolated yields.

BAO^{i}Pr is also involved in this reaction. Thus, when the reduction of excess cyclic ketone with the reagent (2 : 1) was carried out at 25 ℃, 1 equiv of ketone was reduced in a relatively fast rate but the reduction of further equiv of ketone was insignificant. This result indicates that only the isopropoxy moiety of DIBAO^{i}Pr was involved in the reduction with the reagent in a stoichiometric amount at 25 ℃. However, when the reduction was repeated in refluxing EE, the unreacted ketone was also reduced slowly. This result indicated that the isobutyl group of DIBAO^{i}Pr was also involved in this reduction. The reactivity of this reagent toward representative cyclic ketones and the isomeric ratio of the product mixture is summarized in Table 4.

The most striking feature of Table 4 is the stereochemistry of reduction with DIBAO^{i}Pr is apparently dependent on the reaction time. The stereoselectivity increases consistently with increase of reaction time to afford the ther-



modynamically more stable isomer alcohols exclusively, with the exception of camphor which is resistant to reduction under the reaction conditions. This seems to be a phenomenon that must rise where the thermodynamically less stable alcohol isomer, one of the two isomer produced by reduction with DIBAO^{i}Pr, is converted to the more stable one by thermodynamically controlled isomer equilibration *via* a Meerwein-Ponndorf-Verley type reduction.[13b,14]

Conclusion

Al-Alkoxydiisobutylalane (DIBAOR; R=H, Et, *i*-Pr, *t*-Bu) is readily prepared by treating water or alcohol with diisobutylalminum hydride (DIBAH) in ethyl ether (EE) at 0 or 25 °C. The reagents are found to be extremely efficient chemoselective reducing agents in the 1,2-reduction of α,β-unsaturated aldehydes and ketones, and in the competitive reduction between structurally different carbonyl compounds. The most outstanding feature of DIBAOR is that one of the derivatives, DIBAO^{i}Pr, achieves a stereoselective reduction of cyclic ketones to afford the thermodynamically more stable alcohols exclusively. These high selectivities of the reagents should find wide application in organic synthesis.

Experimental Section

All glassware used was dried thoroughly in an oven, assembled hot, and cooled under a stream of dry nitrogen prior to use. All reactions and manipulations of air- and moisture-sensitive materials were carried out using standard techniques for handling air-sensitive materials.[15] All chemicals were commercial products of the highest purity which were purified further by standard methods before use. Ethyl ether (EE) was dried over sodium-benzophenone ketyl and distilled. Diisobutylaluminum hydride (DIBAH) was purchased from Aldrich Chemical Company. GC analyses were performed on a Donam DS 6200 FID chromatograph equipped with a Youngin D520 B computing integrator, using a 10% Carbowax 20 M capillary column (25 m). All GC yields were determined with use of a suitable internal standard and authentic mixture. ^{1}H NMR spectra were recorded on a Varian EM-360 A instrument. ^{27}Al NMR spectra were recorded on a Bruker AMX-300 spectrometer, and chemical shifts are with reference to $[Al(H_2O)_6]^{3+}$.

Preparation of *Al*-alkoxydiisobutylalane (DIBAOR) in EE. The following procedure for the preparation of DIBAOEt (**2**) is illustrative. To an oven-dried, 250 mL flask with a side-arm and a reflux condenser leading to a mercury bubbler were added 35.6 mL of DIBAH (28.4 g, 200 mmol) and 30 mL of EE. It was cooled to 0 °C, and 12.3 mL of ethyl alcohol (9.7 g, 210 mmol) was added dropwise with vigorous stirring. After the hydrogen evolution ceased, the solution of DIBAOEt was diluted with EE to 2 M using a mass cylinder. The ^{27}Al NMR spectrum of the solution showed a broad singlet at δ 152 ppm.

DIBAOH (at 25 °C) and other DIBAOR (at 0 °C) were also prepared by a similar procedure described above and the ^{27}Al NMR spectra showed a broad singlet δ 72 ppm for DIBAOH (**1**), δ 160 for DIBAO^{i}Pr (**3**) and δ 164 for DIBAO^{t}Bu (**4**).

Reduction of α,β-unsaturated carbonyl compounds to allylic alcohols. The following procedure for the reduction of crotonaldehyde with DIBAOEt is representative. An oven-dried, 25-mL flask equipped with a side-arm fitted with a rubber septum, a magnetic stirring bar, and a reflux condenser connected to a mercury bubbler, was charged with 5 mL of a stock solution of DIBAOEt (2 M, 10 mmol) and 0.6 mL of *n*-tridecane (2.5 mmol) as an internal standard. The solution was maintained at 25 °C in a water bath. To this solution was added 0.42 mL of freshly-distilled crotonaldehyde (0.35 g, 5 mmol) with stirring, and the reaction mixture was stirred at that temperature. At the appropriate reaction time, an aliquot was withdrawn and hydrolyzed with 3 N HCl. The aqueous layer was then saturated with potassium carbonate and the ether layer was dried over magnesium sulfate. Gas chromatographic analysis showed the presence of crotyl alcohol as a sole product in yields of 97% at 3 hr and 100% at 6 hr.

In a large scale reaction, crotonaldehyde (2.80 g, 40 mmol) was treated with DIBAOEt (80 mmol) for 6 hrs at 25 °C. Workup as described above, followed by distillation provided crotyl alcohol in 78% yield: bp 121-123°/758 mmHg. GC analysis showed >99% purity and ^{1}H NMR spectrum was identical to that of an authentic sample.

Reduction of cyclic ketones. The following procedure was used to explore the stereoselectivity of this reagent. In a 50 mL, round-bottomed flask was placed 5.0 mL of the 2.0 M solution of the reagent in EE (10 mmol). The flask was maintained at 25 °C by immersion in a water bath. To the flask was added 10 mL of 2-methylcyclohexanone solution in EE (1.0 M in ketone), and the reaction mixture was stirred at 25 °C. After the appropriate time intervals, the reaction aliquot was withdrawn and then quenched by addition of 3 N HCl. The aqueous layer was saturated with $MgSO_4$, and the organic layer was dried over anhydrous K_2CO_3. The isomeric ratio of alcohol product analyzed by GC using a capillary column are listed in Table 1.

Isolation of alcohols. The following procedure is for the larger scale reaction. In the assembly previously described was placed 25 mL of 2.0 M reagent solution (50 mmol). Into the solution was injected 25 mL of a 2.0 M solution of 2-methylcyclohexanone (5.6 g, 50 mmol) in EE, and the reaction mixture was stirred for 7 days at room temperature. The mixture was then hydrolyzed with 50 mL of 3 N HCl, until the gelatinous precipitate was dissolved, and saturated with NaCl. The separated organic layer was washed three times with 3 N NaOH (3×20 mL) and dried over anhydrous K_2CO_3. All the volatile materials were evaporated under reduced pressure to yield almost pure 2-methylcyclohexanol (>98% purity). Fractional distillation gave 4.7 g (82% yield) of essentially pure 2-methylcyclohexanol, bp 166-168 °C (754 mm). GC examination revealed the presence of 4% cis- and 96% *trans*-2-methylcyclohexanol.

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