

Selective reduction of organic compounds with *Al*-acetoxy- and *Al*-trifluoroacetoxydiisobutylalane

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Abstract The new MPV-type reagents, *Al*-acetoxydiisobutylalane (DIBAOAc) and *Al*-trifluoroacetoxydiisobutylalane (DIBAO₂CCF₃), have been prepared and their reducing characteristics in the reduction of selected organic compounds containing representative functional groups have been examined in order to find out a new reducing system with unique applicability in organic synthesis. In general, the reactivity of DIBAO₂CCF₃ appears to be much stronger than that of DIBAOAc, presumably due to the acidity increase by the electron-withdrawing fluorine-substituent. Both reagents reduce aldehydes and ketones relatively slowly, but show an excellent selectivity in 1,2-reduction of α,β -unsaturated carbonyl compounds to produce the corresponding allylic alcohols in an absolutely 100% purity. In addition, the reagents achieve the regioselective cleavage of phenyl- or alkyl-substituted epoxides to the less substituted alcohols in an excellent selectivity. Moreover, both reagents show interesting features in the stereoreduction of cyclic ketones. However, these reagents show a very low or/and no reactivity toward most organic functional groups other than carbonyl and epoxy function.

Keywords *Al*-acetoxydiisobutylalane · *Al*-trifluoroacetoxydiisobutylalane · Selective reduction · Organic functional groups · Stereoreduction

Introduction

As described in the previous article [1], the introduction of acetoxy or trifluoroacetoxy group to diisopinocampheylborane (Ipc₂BH) provides a new class of Meerwein-Ponndorf-Verley (MPV) type reagents, *B*-acetoxydiisopinocampheylborane (Ipc₂BOAc) and *B*-trifluoroacetoxydiisopinocampheylborane (Ipc₂BO₂CCF₃), which possess unique reducing characteristics showing an excellent selectivity in the reduction of carbonyl compounds. Especially noteworthy is that the reactivity of Ipc₂BO₂CCF₃ is much higher than that of Ipc₂BOAc. We believe that the strong electron-withdrawing fluorine substituent in acetoxy group increases the acidity of the reagent and makes it stronger. This phenomenon strongly indicates that the reaction proceeds via the six-membered transition state in which the Lewis acidic boron atom coordinates to the carbonyl oxygen followed by the hydride transfer from isopinocampheyl moiety to the carbonyl acceptor, quite similar to the mechanism which is generally accepted in the original MPV reaction using aluminum alkoxides [2].

These results attracted us. It seems desirable to design the acetoxy-substituted alane derivatives, *Al*-acetoxydiisobutylalane (DIBAOAc) and *Al*-trifluoroacetoxydiisobutylalane (DIBAO₂CCF₃), and to characterize the Lewis acidity effect between these two derivatives in the reduction of organic functionalities. Accordingly, we examined the reducing characteristics of both alane derivatives in the reduction of organic compounds containing representative

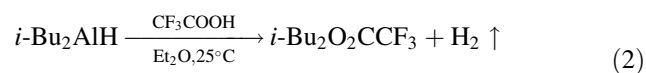
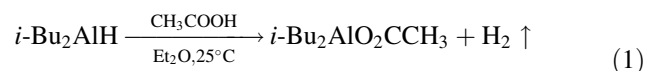
We dedicate this manuscript to Prof. Jack Harrowfield and Dr. Jacques Vicens in celebration of their 65th birthdays.

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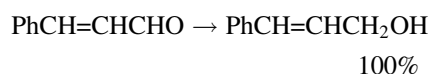
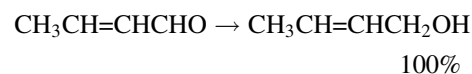
functional groups and compared their reactivities in order to find out a new MPV type reducing system with unique applicability in organic synthesis [3–12].

Results and discussion

DIBAOAc and DIBAO₂CCF₃ can be prepared easily by a simple reaction of diisobutylaluminium hydride (DIBAH) with acetic acid or trifluoroacetic acid, respectively in Et₂O (Eqs. 1 and 2).



The reactivity of DIBAOAc and DIBAO₂CCF₃ toward some representative aldehydes and ketones in Et₂O at 25 °C was examined, and the results are summarized in Table 1. As shown in the Table, DIBAOAc showed very little reactivity toward simple aldehydes and ketones: even excess amount of the reagent (2 equiv) could not achieve a complete reduction within 72 h at 25 °C. However, DIBAO₂CCF₃ exhibited a much higher reactivity under the same reaction conditions. Thus, most aldehydes and ketones examined were reduced to the corresponding alcohols by excess DIBAO₂CCF₃ in 3–5 days at 25 °C. A similar reactivity difference was also detected in the reaction of α,β -unsaturated aldehydes such as crotonaldehyde and cinnamaldehyde. Thus, for example, excess DIBAOAc (2 equiv) reduced crotonaldehyde to crotyl alcohol in 24 h at 25 °C, whereas DIBAO₂CCF₃ readily reduced it within 3 h under the same reaction conditions. In addition, especially noteworthy is the chemoselectivity observed in these reactions. Both reagents achieved a clean 1,2-reduction to show an essentially perfect selectivity: products are the corresponding allylic alcohols in 100% purity.



The most fascinating feature of the reagents seems to be the results obtained in the reaction of epoxides. DIBAOAc reduced both aliphatic and aromatic epoxides examined in Et₂O at 0 °C to produce the substituted alcohol exclusively by trapping β -hydrogen from isobutyl groups of the reagent at the site best able to accommodate a carbocation ion. The regioselectivity reaches 100% for aliphatic epoxides and

Table 1 Reaction of simple aldehydes and ketones with *Al*-acetoxy- and *Al*-trifluoroacetoxydiisobutylalane (DIBAOAc and DIBAO₂CCF₃) in ethyl ether at 25 °C

Compound	Reagent/ Compd	Time (h)	Yield of alcohol (%) ^a	
			DIBAOAc	DIBAO ₂ CCF ₃
Hexanal	1.1	6	13	30
		24	30	35
		72	35	47
	2.0	6	25	35
		24	47	58
		72	60	76
Benzaldehyde	1.1	6	25	92
		24	32	96
		72	41	99
	2.0	3	28	95
		6	35	99.9, 75 ^b
		24	42	99.9
2-Heptanone	1.1	6	45	73
		24	52	78
		72	56	82
	2.0	6	70	85
		24	82	96
		72	84	99
Acetophenone	1.1	6	30	46
		24	35	53
		72	44	58
	2.0	6	35	73
		24	64	86
		72	70	95
Benzophenone	1.1	6	2	40
		24	5	48
		72	8	55
	2.0	6	24	70
		24	38	85
		72	45	92
Crotonaldehyde ^d	1.1	3	40	98
		6	55	99
		24	80	99
	2.0	72	99	
		1	31	97
		3	75	99.9, 93 ^c
Cinnamaldehyde ^d	1.1	6	96	
		24	99.9	
		3	5	55
	1.1	6	3.6	79
		24	60	88
		72	69	90

Table 1 continued

Compound	Reagent/ Compd	Time (h)	Yield of alcohol (%) ^a	
			DIBAOAc	DIBAO ₂ CCF ₃
	2.0	3	10	75
		6	56	88
Hexanal	1.1	6	13	30
		24	30	35

^a Determined by GC using a suitable internal standard. Concentration of each compound examined was 0.5 M

^b Isolated yield on distillation

^c Isolated yield by chromatography

^d The products are the corresponding alkyl alcohols in 100% purity

94% for aromatic one such as styrene oxide. Furthermore, the reagent discriminates between the phenyl- and the alkyl group-attached carbon site in the ratio of 92:8 in the reaction of *trans*- β -methylstyrene oxide (Table 2).

In addition, as listed in Table 3, DIBAO₂CCF₃ reduced both aliphatic and aromatic epoxides at a much faster rate than DIBAOAc: the reagent with 10% excess amount reduced them examined completely within 1 h at 0 °C to produce the more substituted alcohol exclusively. The regioselectivity achieved by DIBAO₂CCF₃ is almost same with that by DIBAOAc. The reagent also discriminates

between the phenyl- and the alkyl group-substituted epoxy carbon site (i.e., 94:6).

Such an anti-Markovnikov reductive opening of epoxides by MPV type reducing agents has previously been exemplified with (*i*PrO)₃B [13] and *Al*-fluorodiisobutylalane (DIBAF) [14]. Such reagents also showed an excellent regioselectivity, but each reagent possesses its own limitations in the reduction procedure, such as a relatively low reactivity, requirement of sophisticated experimental technique for preparing reagent, etc.

Both derivatives also reduced acid chloride to produce the corresponding aldehydes and alcohols, but it seems to be of low synthetic utility (Table 4).

The reactivity of the reagents toward other functional compounds was also examined and the results are summarized in Table 5. As shown in the Table, both derivatives exhibited no reactivity toward carboxylic acids, esters, amides, nitriles and sulfur compounds except for sulfoxide. Dimethyl sulfoxide was readily reduced to dimethyl sulfide. Such a mild reducing characteristics of the reagents makes it possible the chemoselective reduction of aldehydes, ketones or epoxides in the presence of such inert compounds.

Finally, we applied both reagents to the reduction of representative cyclic ketones and examined its stereochemistry. As shown in Table 6, the reactivity difference between DIBAOAc and DIBAO₂CCF₃ was also appeared

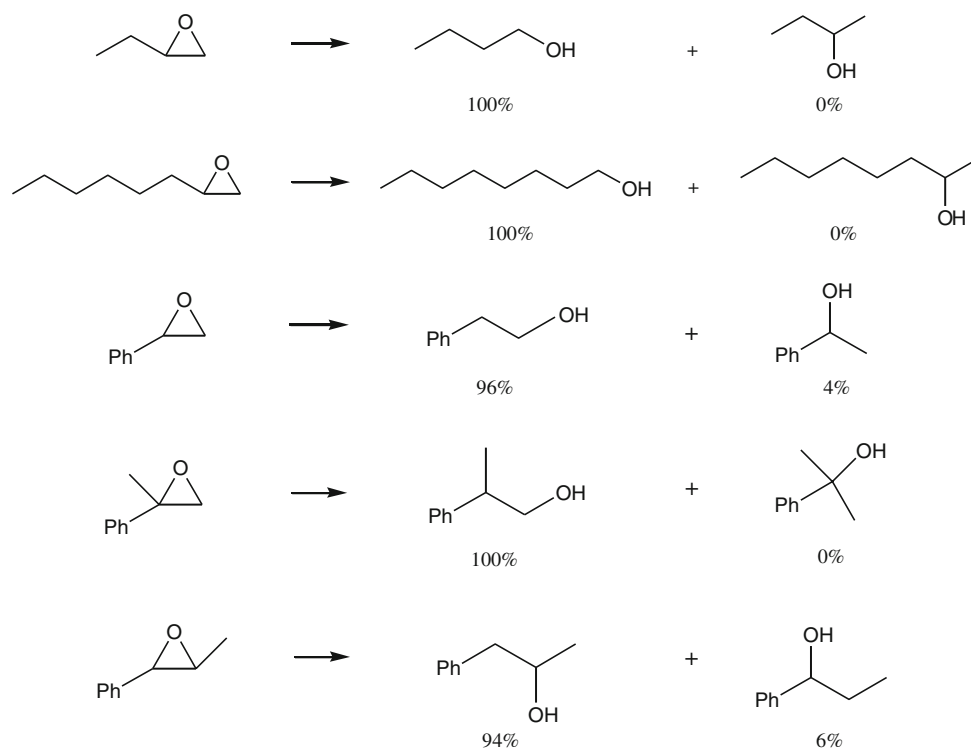


Table 2 Reaction of epoxides with DIBAOAc in ethyl ether at 0 °C^a

Epoxides	Reagent/ Compd	Time (h)	Yield (%) ^b	Ratio of products (%) ^c	
1,2-Epoxybutane	1.1	6	58	100	1-Butanol + 2-Butanol 0
		24	80	100	0
	2.0	1	75	100	0
		3	85	100	0
		6	99	100	0
1,2-Epoxyoctane	1.1	6	41	100	1-Octanol + 2-Octanol 0
		24	65	100	0
	2.0	3	46	100	0
		6	78	100	0
		24	99.9	100	0
Styrene oxide	1.1	3	35	94	2-Phenylethanol + 1-Phenylethanol 6
		6	44	94	6
		24	72	94	6
		72	76	94	6
	2.0	3	55	94	6
		6	62	94	6
		24	83	94	6
		72	99	94	6
α -Methylstyrene oxide	2.0	3	63	100	2-Phenyl-1-propanol + 2-Phenyl-2-propanol 6
		6	72	100	6
		24	86	100	6
		72	100	100	6
<i>Trans</i> - β -Methylstyrene oxide	2.0	6	75	92	1-Phenyl-2-propanol + 1-Phenyl-1-propanol 8
		24	91	92	8
		72	99	92	8

^a Concentration of each compound examined was 0.5 M

^b Analyzed by GC using a suitable internal standard

^c Normalized

in this cycloalkanone reduction: DIBAO₂CCF₃ is much higher than DIBAOAc. DIBAO₂CCF₃ readily reduced all the cyclic ketones examined at 25 °C except for 2-*tert*-butylcyclohexanone and camphor. Particularly, the distinct rate difference between 2-methyl- and 2-*tert*-butylcyclohexanone is remarkable: 2-methylcyclohexanone was readily reduced, but 2-*tert*-butylcyclohexanone was quite inert to the reagents. These results clearly indicate that the steric requirement around the coordination sphere is also an important factor upon the reduction rate. However, notwithstanding the reactivity difference between these two derivatives, the stereochemistry of the product alcohols obtained in the reduction of all the cyclic ketones examined is consistently the thermodynamically more stable epimer [7, 13].

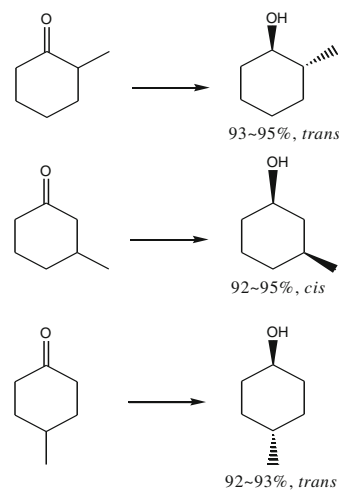


Table 3 Reaction of epoxides with DIBAO₂CCF₃ in ethyl ether at 0 °C^a

Epoxides	Reagent/Compd	Time (h)	Yield (%) ^b	Ratio of products(%) ^c	
				1-Butanol	+ 2-Butanol
1,2-Epoxybutane	1.1	0.5	95	100	0
		1	100	100	0
1,2-Epoxyoctane	1.1	0.5	99.9	99	1
				1-Octanol	+ 2-Octanol
Styrene oxide	1.1	0.5	100	96	4
				2-Phenylethanol	+ 1-Phenylethanol
α -Methylstyrene oxide	1.1	0.5	95	99	1
		1	99.9, 91 ^d	99	1
<i>Trans</i> - β -Methylstyrene oxide	1.1	0.5	96	94	6
		1	100	94	6
				1-Phenyl-2-propanol	+ 1-Phenyl-1-propanol

^a Concentration of each compound examined was 0.5 M

^b Analyzed by GC using a suitable internal standard

^c Normalized

^d Isolated yield by chromatography

Table 4 Reaction of representative acid chlorides with DIBAOAc and DIBAO₂CCF₃ in ethyl ether at 25 °C^a

Compound	Reagent/Compd	Time (h)	Products (%) ^b			
			DIBAOAc		DIBAO ₂ CCF ₃	
			Aldehyde	Alcohol	Aldehyde	Alcohol
Hexanoyl chloride	1.1	1	20	15	22	14
		6	25	30	28	20
		24	21	35	29	24
	2.0	1	25	35	21	15
		6	28	45	49	20
		24	40	65	57	35
Benzoyl chloride	1.1	1	3	5	20	2
		6	4	21	24	3
		24	10	33	28	4
	2.0	1	4	11	30	3
		6	10	25	35	4
		24	12	54	37	5

^a Concentration of each compound examined was 0.5 M

^b Analyzed by GC using a suitable internal standard

Conclusion

The reducing characteristics of the new MPV-type reagents, DIBAOAc and DIBAO₂CCF₃, are now fully understood. In general, both reagents are extremely mild, showing only reactivity toward aldehydes, ketones and epoxides. The reactivity of DIBAO₂CCF₃ appears to be much higher than that of DIBAOAc. Especially, DIBAO₂CCF₃ exhibits a unique reducing applicability in organic synthesis. The reagent achieved a clean 1,2-reduction of α,β -unsaturated aldehydes and an excellent regioselective cleavage of phenyl- or alkyl-substituted epoxides. In addition, the reagent

produced the thermodynamically more stable alcohol epimer in high stereoselectivity from the reduction of alkyl-substituted cycloalkanones.

With organic research undertaking the synthesis of structures of increasing complexity, there was an evident and growing need for reagents possessing a high degree of selectivity. Therefore, this systematic study could provide the organic chemist with a more complete spectrum of reagents for selective reductions.

Experimental section

All glassware used in this study was predried at 140 °C for at least 9 h, assembled hot, and cooled under a stream

Table 5 Reaction of other functional compounds with DIBAOAc and DIBAO₂CCF₃ in ethyl ether at 25 °C^a

Compound	Reagent/Compd	Time (h)	Reduction yield (%) ^b	
			DIBAOAc	DIBAO ₂ CCF ₃
Hexanoic acid	2.0	24	0	1 ^c
Benzoic acid		72	0	36 ^c
Ethyl caproate	2.0	72	0	0
Ethyl benzoate	2.0	24	0	1 ^c
Phenyl acetate		72	0	25 ^c
Caproamide	2.0	72	0	0
Benzamide	2.0	72	0	0
<i>N,N</i> -Dimethylbenzamide	2.0	70	0	0
Hexanenitrile	2.0	72	0	0
Benzonitrile	2.0	72	0	0
Phenyl sulfide	2.0	72	0	0
Phenyl sulfone	2.0	72	0	0
Dimethyl sulfoxide	2.0	3	78 ^d	99.8 ^d
		6	99 ^d	

^a Concentration of each compound examined was 0.5 M

^b Analyzed by GC using a suitable internal standard

^c Product is hexanol

^d Product is dimethyl sulfide

of dry N₂ prior to use. All reactions were performed under a dry N₂ atmosphere. All chemicals used were commercial products of the highest purity available, which were further purified by standard methods before use. Et₂O was distilled from sodium-benzophenone ketyl prior to use. Gas chromatographic analyses were carried out with a Varian 4400 chromatograph using DB-Wax and HP-FFAP capillary columns (30 m).

Preparation of *Al*-Acetoxy- and *Al*-trifluoroacetoxydiisobutylalane (DIBAOAc and DIBO₂CCF₃)

Into an oven-dried, 100 mL flask with a sidearm equipped with a downward-directed, water-cooled condenser leading to a mercury bubbler, 11 g of diisobutylaluminum hydride (DIBAH, 75 mmol) was injected using a double-ended needle and diluted with Et₂O to be 2.0 M. The flask was inserted into a water-circulating bath and maintained at 25 °C. To this solution was added 15 mL of a 5.0 M solution of acetic acid (75 mmol) in Et₂O dropwise. After the complete evolution of hydrogen gas, the solution was diluted with Et₂O to be 1.5 M. The ²⁷Al NMR spectra of the solution showed a broad singlet centered at δ3.2 ppm (DIBAOAc) and δ1.5 ppm (DIBAO₂CCF₃) relative to Al(H₂O)₆³⁺.

General procedure for reduction of organic compounds

The reaction of benzaldehyde with 2 equiv of DIBAO₂CCF₃ is illustrative. An oven-dried, 50 mL flask, fitted with a sidearm and a bent adapter connected to a mercury bubbler, was charged with 0.53 g of benzaldehyde (5 mmol), 4.5 mL of Et₂O and tridecane as an internal

standard. The solution was maintained in a circulating bath at 25 °C. To this was added 6.7 mL of a stock solution of DIBAO₂CCF₃ (10.0 mmol) in Et₂O with stirring. At the appropriate time interval (i.e., 1, 3, 6 and 24 h), an aliquot (ca. 1 mL) was withdrawn, and the mixture was hydrolyzed with 3 *N* HCl for 2 h. The aqueous layer was saturated with K₂CO₃ and the organic layer was dried over anhydrous MgSO₄. The organic layer was then subjected to gas chromatographic analysis to yield 95% of benzyl alcohol at 3 h and 99.9% at 6 h.

Isolation of reduction products

The following procedure is representative for isolation of reduction products on distillation. In the assembly previously described was placed 3.18 g of benzaldehyde (30 mmol) in 16 mL of Et₂O and the solution was maintained in a circulating bath at 25 °C. Into the solution was injected 40 mL of a stock solution of DIBAO₂CCF₃ (60 mmol) in Et₂O with stirring and the reaction mixture was stirred for 6 h. The mixture was then quenched with 3 *N* HCl. The aqueous layer was saturated with NaCl. The separated organic layer was dried over anhydrous MgSO₄. The solvent was distilled out under reduced pressure and a careful fractional distillation gave 2.43 g (75% yield) of essentially pure benzyl alcohol.

The following procedure is illustrative for isolation of product alcohols by column chromatography. In the assembly was placed 0.35 g of crotonaldehyde (5 mmol) in 2.2 mL of Et₂O and the flask was maintained in a circulating bath at 25 °C. Into the flask was injected 6.7 mL of a stock solution of DIBAO₂CCF₃ (10 mmol) in Et₂O with stirring, and the reaction mixture was stirred for 3 h. The mixture was then hydrolyzed with 3 *N* HCl. The aqueous

Table 6 Stereochemistry in the reduction of representative cyclic ketones with DIBAOAc and DIBAO₂CCF₃ in ethyl ether at 25 °C^{a,b}

Compound	Reagent/ Compd	Time (h)	DIBAOAc		DIBAO ₂ CCF ₃	
			Yield of alcohol (%)	Ratio of stable isomer (%) ^c	Yield of alcohol (%)	Ratio of stable isomer (%) ^c
2-Methylcyclohexanone	1.1	3	15	78 ^d	65	93 ^d
		6	18	78	72	93
		24	35	88	85	94
		72	45	88	96	95
	2.0	3	22	77	85	93
		6	35	87	88	93
		24	60	87	95	94
		72	78	87	99	94
3-Methylcyclohexanone	1.1	3	10	92 ^e	84	94 ^e
		6	20	92	86	94
		24	55	92	90	94
		72	75	92	98	95
	2.0	3	20	93	87	90
		6	39	93	92	92
		24	85	93	96	92
		72	95	93	99	92
4-Methylcyclohexanone	1.1	3	15	89 ^f	65	91 ^f
		6	35	89	75	93
		24	70	90	92	93
		72	85	90	96	93
	2.0	3	20	92	92	92
		6	48	92	95	92
		24	94	92	99	92
		72	94	92	99	93
2- <i>tert</i> -Butylcyclohexanone	2.0	24	1	1 ^g	30	15 ^g
		72	14	3	41	25
4- <i>tert</i> -Butylcyclohexanone	1.1	6	20	90 ^h	90	98 ^h
		24	65	93	95	98
		72	83	93	96	98
	2.0	3	21	94	92	97
		6	30	94	94	98
		24	80	94	96	98
3,3,5-Trimethylcyclohexanone	1.1	6	15	95 ⁱ	28	95 ⁱ
		24	35	98	40	98
		72	40	98	52	98
		216			95	98
	2.0	3	13	85	85	94
		6	22	95	95	97
		24	50	95	96	98
		72	65	96	99.9	98
Norcamphor	1.1	24	15	75 ^j	60	85 ^j
		72	30	76	80	85
		216			95	85
	2.0	3	8	71	85	81
		6	10	75	91	82

Table 6 continued

Compound	Reagent/ Compd	Time (h)	DIBAOAc		DIBAO ₂ CCF ₃	
			Yield of alcohol (%)	Ratio of stable isomer (%) ^c	Yield of alcohol (%)	Ratio of stable isomer (%) ^c
Camphor	2.0	24	25	75	95	83
		72	40	75	100	83
		72	1	73 ^k	30	75 ^k
		216			35	78

^a Concentration of each compound was 0.5 M

^b Determined by GC

^c Normalized

^d *Trans* isomer

^e *Cis* isomer

^f *Trans* isomer

^g *Trans* isomer

^h *Trans* isomer

ⁱ *Cis* isomer

^j *Exo* isomer

^k *Endo* isomer

layer was saturated with NaCl. The separated organic layer was dried over anhydrous MgSO₄. The solvent was removed under reduced pressure and the product was chromatographed on a column of silica gel using a mixture of hexane:ethyl acetate (10:1) as eluent to afford 0.34 g of crotyl alcohol (93%). The product was characterized by PMR.

Reduction of cyclic ketones

The following procedure was used to explore the stereoselectivity of DIBAO₂CCF₃. In the usual setup, the flask containing 5 mmol of ketone examined was reacted with 10 mmol of the reagent in Et₂O (a total of 10 mL reaction mixture) at 25 °C. At the appropriate time intervals, an aliquot was withdrawn and hydrolyzed with 3 N HCl. The aqueous layer was saturated with K₂CO₃ and the organic layer was dried over anhydrous MgSO₄. The organic layer was then subjected to gas chromatographic analysis.

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For other diisobutylalane derivatives

See the review papers, some references cited in

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