β,β-Difluoro-α-phenylvinyl sulfide 1 (1.0 mmol) was added dropwise at room temperature and then stirred for further 4 hr. The reaction mixture was poured on water (10 m*l*) and extracted with ethyl acetate (10 m*l*×2). The ethyl acetate solution was dried and chromatographed on SiO_2 column. Elution with a mixture of hexane and ethyl acetate (20 : 1) provided **3e** in 80% yield. **3e** : colorless oil; ^{1}H NMR ($CDCl_3$) δ 7.78-7.02 (m, 10H), 4.48 (q, J=7.3 Hz, 2H), 4.10 (q, J=7.3 Hz, 2H); MS, m/e (relative intensity) 408 (M^+, 54), 325 (48), 309 (100), 225 (10), 197 (32); IR (neat) 3050, 3000, 1630, 1450, 1290, 1170, 970, 770, 750, 700 cm^{-1}.

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7. Spectroscopic data of **2b**: colorless oil; ^{1}H NMR ($CDCl_3$) δ 7.75-7.10 (m, 10H), 4.25 (q, J=7.3 Hz, 2H), 1.35 (t, J=7.3 Hz, 3H); MS, m/e (relative intensity) 274 (M^+, 86), 245 (100), 217 (95), 197 (48), 121 (95), 77 (71); IR (neat) 3000, 1640, 1570, 1470, 1230, 1150, 760, 690 cm^{-1}.
8. Spectroscopic data of **4b**: colorless oil; ^{1}H NMR ($CDCl_3$) δ 7.50-7.15 (m, 10H), 4.90 (s, 1H), 4.10 (q, J=7.3 Hz, 2H), 1.15 (t, J=7.3 Hz, 3H); MS, m/e (relative intensity) 272 (M^+, 42), 199 (100), 135 (20), 109 (24), 91 (27), 77 (29); IR (neat) 3000, 1730, 1430, 1150, 760, 700 cm^{-1}.
9. Spectroscopic data of **5**: mp. 109-110 ℃ ; ^{1}H NMR ($CDCl_3$) δ 7.40-7.20 (m, 10H), 5.15 (s, 1H), 2.99 (s, 3H), 2.91 (s, 3H), MS, m/e (relative intensity) 271 (M^+, 15), 199 (100), 162 (8), 134 (34), 72 (17); IR (neat) 3000, 1640, 1400, 1130, 750, 710 cm^{-1}.

Diisopinocampheylchloroborane as a Highly Selective Reducing Agent for the Conversion of α,β-Unsaturated Aldehydes and Ketones to the Corresponding Allylic Alcohols

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Chiral diisopinocampheylchloroborane (^{d}Ipc$_2$BCl and ^{l}Ipc$_2$BCl)[1] has proven to be extremely efficient for the asymmetric reduction of a wide variety of ketones to obtain chiral alcohols in high ee.[2-6] Most organic functional groups, except for aldehydes, ketones[2-6] and epoxides,[7] are compatible with the reagent. Moreover, the ready availability of both the enantiomers, simple reaction conditions, easy work-up procedure, and completely recovery of the chiral auxiliary α-pinene[7] make this reagent especially attractive. The mechanism of the reduction is explained *via* a cyclic boatlike transition state.[4] This fascinating reagent attracted us to investigate its general reducing characteristics in greater detail. In the course of this investigation, we found that Ipc$_2$BCl readily reduces crotonaldehyde, an α,β-unsaturated aldehyde, to the corresponding allylic alcohol at 0° without any detectable 1,4-reduction product. Selective 1,2-reduction of α,β-unsaturated aldehydes and ketones with metal hydride reducing agents is often difficult to achieve in organic synthesis due to competing 1,2- *vs.* 1,4-attack by hydride.[8] Among the various reducing systems which have been devised for this purpose, diisobutylaluminum hydride (DIBAH),[9] lithium aluminum hydride (LAH),[10] 9-borabicyclo[3.3.1]nonane (9-BBN),[11] lithium *n*-butylborohydride,[12] and sodium borohydride in aqueous methanol containing rare earth chloride[13] are generally the most efficient and convenient.[14] However, these can by no means be adapted as a very general procedure.[11,13,15,16] Accordingly, it appeared desirable to generalize the reagent Ipc$_2$BCl as an ideal reducing agent for the selective reduction of α,β-unsaturated aldehydes and ketones to the corresponding allylic alcohols.

The reduction was carried out by the addition of 10% excess Ipc$_2$BCl in pentane to the aldehyde in pentane at 0° and to the ketone in pentane at room temperature.

Reduction of simple conjugated aldehydes, such as crotonaldehyde, 2-hexenal and cinnamaldehyde, afforded exclusively the corresponding allylic alcohols, resulting only from 1,2-reduction. Acyclic enones, such as 3-penten-2-one, benzalacetone and chalcone, were also selectively converted into the corresponding allylic alcohols in essentially quantitative yield at room temperature. Excess reagent (two equivalents) did not affect the selectivity, but accelerated the reduction rate. 2-cyclohexenone was converted to 2-cyclohexenol in quantitative yields. Even 2-cyclopentenone, known for its susceptibility to undergo conjugate reduction, was clearly converted to the desired 2-cyclopentenol in quantitative yield. Similarly, isophorone was readily reduced to 3,5,5-trimethyl-2-cyclohexen-1-ol.

Table 1. Reduction of α,β-Unsaturated Alehydes and Ketones with Diisopinocampheylchloroborane in Pentane[a,b]

Compound	Time, h	Product ratio, 1,2 : 1,4	Yield, %[c]
Crotonaldehyde	3	100 : 0	>99.9
2-Hexenal	3	100 : 0	>99.9
Cinnamaldehyde	6	100 : 0	94
	12	100 : 0	>99.9
3-Penten-2-one	6	100 : 0	85
	24	100 : 0	>99.9
Benzalacetone	24[d]	100 : 0	50
	6	100 : 0	96
	24	100 : 0	>99.9
Chalcone	24	100 : 0	90
	48	100 : 0	95
	72	100 : 0	>99.9
	24[e]	100 : 0	100
2-Cyclohexenone	1	100 : 0	95
	3	100 : 0	>99.9
2-Cyclopentenone	1	100 : 0	90
	3	100 : 0	>99.9
Isophorone	6	100 : 0	98
	12	100 : 0	100
	6[e]	100 : 0	100

[a] A 1.1 : 1 ratio for reagent : compound was utilized, except where otherwise indicated. [b] Reacted at 0° for the aldehydes and at 25° for the ketones, except where otherwise indicated. [c] GC yields. [d] Reacted at 0°. [e] Two equivalents of reagent utilized.

Results summarized in Table 1 clearly reveal that the reagent in really an ideal reducing agent for the selective reduction of α,β-unsaturated aldehydes and ketones to the corresponding allylic alcohols.[17] The selectivity is 100%. Furthermore, Ipc_2BCl is extremely mild. Even acid chloride, the most susceptible functional group, is compatible.[18] This represents major advantage of Ipc_2BCl over the more conventional reagents for the reduction of enals and enones to allylic alcohols.

The following procedure for the reduction of crotonaldehyde to crotyl alcohol is representative. A clean oven-dried 25-mL flask equipped with a side arm fitted a rubber stopple, magnetic stirring bar, and a reflux condenser connected to a mercury bubbler was cooled down to room temperature with nitrogen. Pentane (1 mL) was injected into the reaction flask followed by 0.42 mL (5 mmol) of crotonaldehyde (freshly distilled) and 0.60 mL (2.5 mmol) of *n*-tridecane. The reaction flask was cooled to 0° (ice bath) and 2.8 mL (5.6 mmol) of a 2 M Ipc_2BCl solution in pentane[19] was added. The mixture was stirred at 0° for 3 h. Then the reaction mixture was hydrolyzed and oxidized ($NaOH$-H_2O_2, 25°, 2 h). The aqueous layer was saturated with potassium carbonate and the dry pentane layer was subjected to GC analysis on a 15% Carbowax 20 M column, 12 ft×0.125 in., indicating the presence of crotyl alcohol as a sole product in >99.9% yield.

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