

irreversible *cis-trans* isomerization of 2.

The photoreduction of 1 in hydrogen donor solvents takes a completely different course in the presence of photosensitizers such as benzophenone. Under these conditions, the primary reaction is reduction to 1,3-dibenzoylpropane.<sup>3</sup>

Radical trapping experiment and C-3 methyl substituent effect are under investigation to obtain further information on the arguments in 1,2- vs. 1,3-bond cleavage of 1,2-dibenzoyl-3-phenylcyclopropane.

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### *B-t*-Butoxydiisopinocampheylborane as a Highly Chemoselective Reducing Agent for Aldehydes

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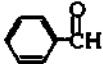
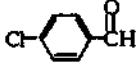
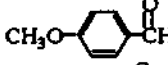
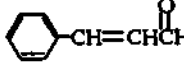
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Very recently, we reported that *B*-hydroxydiisopinocampheylborane ( $\text{Ipc}_2\text{BOH}$ ),<sup>1</sup> a newly synthesized reagent, is an exceptionally mild, highly selective reducing agent for the reduction of only the aldehyde group in the presence of keto and all other functional groups. The reagent has proven to be superior to all of earlier reagents.<sup>2</sup> In continuation of our efforts to explore new reducing systems for such transformations, we prepared a series of *B*-alkoxydiisopinocampheylborane ( $\text{Ipc}_2\text{BOR}$ ) and examined the reducing action toward general organic functional groups. In the course of this systematic study, we found that *B-t*-butoxydiisopinocampheylborane ( $\text{Ipc}_2\text{BO}^t\text{Bu}$ ) reduces only the aldehydes cleanly, while all common organic functional groups are not affected. Herein, we report the results for such selective reduction of aldehydes by  $\text{Ipc}_2\text{BO}^t\text{Bu}$  in pentane.

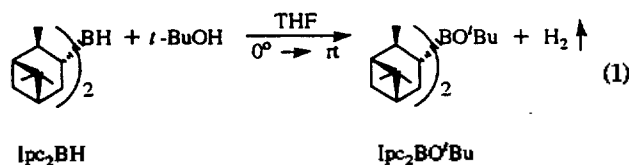
The reagent can be readily prepared by alcoholysis of di-

**Table 1.** Reduction of Aldehydes to Alcohols with  $\text{Ipc}_2\text{O}^t\text{Bu}$  in Pentane at 25°<sup>a</sup>

Substrate	Time (h)	Yields (%) <sup>b</sup>
$\text{CH}_3(\text{CH}_2)_2\text{CHO}$	1	100
$\text{CH}_3(\text{CH}_2)_4\text{CHO}$	3	100
	3	100
	3	100
	3	100
$\text{CH}_3\text{CH}=\text{CHCHO}$	3	100
$\text{CH}_3(\text{CH}_2)_2\text{CH}=\text{CHCHO}$	6	100
	12	100

<sup>a</sup>Ten % excess reagent was utilized. Reaction mixtures were ca. 1 M in substrates. <sup>b</sup>Yields of the corresponding alcohols determined by GLC using appropriate internal standard.

isopinocampheylborane ( $\text{Ipc}_2\text{BH}$ )<sup>3</sup> in THF solution (Eq. 1). After the complete evolution of hydrogen, the solvent was distilled out under reduced pressure and replaced with pentane.



$\text{Ipc}_2\text{BO}^t\text{Bu}$  is an effective reagent for the reduction of a wide variety of aldehydes in pentane at 25°. Like the case of  $\text{Ipc}_2\text{BCl}^3$  and  $\text{Ipc}_2\text{BOH}$ ,<sup>1</sup> the formation of an intermediate alkoxyborane is accompanied by the elimination of  $\alpha$ -pinene. The treatment of the reaction mixture with acetaldehyde (liberation of the second  $\alpha$ -pinene) followed by addition of aqueous sodium hydroxide affords the alcohol product.<sup>4</sup>

The transformation of representative aldehydes to the corresponding alcohol with 10% excess reagent at 25° in pentane is listed in Table 1. A wide variety of aldehydes are reduced completely in less than 6 h.  $\alpha,\beta$ -Unsaturated aldehydes are also reduced to the corresponding allylic alcohols cleanly.

The chemoselectivity of this reagent was tested with several representative aldehyde-ketone pairs and aldehyde-other reactive compound pairs in competition experiments. Equimolar amounts of two compounds were allowed to compete for a limited quantity of  $\text{Ipc}_2\text{BO}^t\text{Bu}$  (1 equivalent). A standard solution of the reagent (ca. 2 M) in pentane maintained at 25°.

After 6 h, the mixture was treated with acetaldehyde and hydrolyzed with aqueous sodium hydroxide. The results ob-

**Table 2.** Selective Reduction of Aldehyde Groups in the presence of Keto and Other Functional Groups with  $\text{Ipc}_2\text{O}^t\text{Bu}$  in Pentane at 25 $^\circ$ 

Starting mixture	Time (h)	Ratio of reduction products <sup>b</sup>
Butanal/Cyclohexanone	1	100 : 0
Hexanal/Cyclohexanone	6	100 : 0
Hexanal/2-Heptanone	6	100 : 0
Hexanal/Acetophenone	6	100 : 0
Hexanal/Benzophenone	6	100 : 0
Benzaldehyde/Hexanal	6	60 : 40
Benzaldehyde/Cyclohexanone	6	100 : 0
Benzaldehyde/2-Heptanone	6	100 : 0
<i>p</i> -Anisaldehyde/Cyclohexanone	6	>99.9 : trace
Hexanal/Hexanoyl chloride	6	100 : 0
Hexanal/Benzoyl chloride	6	100 : 0
Hexanal/1,2-Butylene oxide	6	100 : 0

<sup>a</sup>Reaction mixture were ca. 1 M in substrates. One equivalent of reagent was utilized for competitive reduction of equimolar mixture of two carbonyl compounds. <sup>b</sup>Normalized ratio determined by GLC with appropriate internal standard; the total yields of product alcohols were  $\geq 99.9\%$ .

tained by GC analysis of the reaction mixture with internal standard are summarized in Table 2.

Both aliphatic and aromatic aldehydes examined are selectively reduced in the presence of simple ketones: hexanal is selectively reduced in the presence of even cyclohexanone. Likewise, benzaldehyde can be selectively reduced in the presence of cyclohexanone. Even more important is the chemoselective discrimination between hexanal and acid chloride. Furthermore, epoxides are inert to the reagent. Consequently, the reagent permits the selective reduction of aldehyde groups in the presence of nearly all other functional groups. Although  $\text{Ipc}_2\text{BOH}$  has proven to be the most excellent reagent in its ability to discriminate between an aldehyde and a ketone, the reduction rate is quite slow: the reagent requires a 24 h reaction at 25 $^\circ$  for completion.<sup>1</sup> Consequently, a remarkable inertness of  $\text{Ipc}_2\text{BO}^t\text{Bu}$  toward most of the functional groups, coupled with a superior selectivity (100%) and a high reactivity (6 h at 25 $^\circ$ ) in the reduction of aldehydes provide an extremely useful method for such selective reduction.

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## Direct Synthesis of $\alpha,\alpha$ -Bis(silyl)toluenes

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Since the direct synthesis of methylchlorosilanes from elemental silicon and methyl chloride catalyzed by copper was invented by Rochow in 1940's,<sup>1</sup> direct reactions of metallic silicon with various alkyl chlorides have been studied extensively.<sup>2</sup> However the direct reaction of benzyl chloride has not been reported yet, because benzyl chloride decomposes rapidly when contact with Si-Cu contact mass at temperature above 150  $^\circ\text{C}$ .<sup>3</sup> We recently reported the direct synthesis of 2,2-dichloro-2-silaindan by reacting  $\alpha,\alpha'$ -dichloro-*o*-xylene with elemental silicon (eq. 1).<sup>4</sup> It was first example that benzylic chloride was used in the direct synthesis. We also found that hydrogen chloride addition to organic chlorides in the direct synthesis suppressed the decomposition of starting compounds and gave the Si-H containing silane products mainly.

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