# Diisopinocampheylborane

**Diisopinocampheylborane** is an <u>organoborane</u> that is useful for <u>asymmetric synthesis</u>. This colourless solid is the precursor to a range of related <u>reagents</u>. The compound was reported in 1961 by Zweifel and <u>Brown</u> in a pioneering demonstration of asymmetric synthesis using boranes. The reagent is mainly used for the synthesis of <u>chiral</u> secondary alcohols.

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# **Preparation**

Diisopinocampheylborane was originally prepared by hydroboration of excess  $\alpha$ -pinene with borane, but it is now more commonly generated from borane-methyl sulfide (BMS).

The compound can be isolated as a solid. However, because it is quite sensitive to water and air, this reagent is often generated in situ and used as a solution.

Diisopinocampheylborane is monomeric, in contrast to diborane and many of its less bulky analogues.

## **Reactions**

Oxidation of diisopinocampheylborane with basic hydrogen peroxide gives isopincampheol. Methanolysis gives methoxydiisopinocampheylborane

### **Hydroboration**

Because of the large <u>size</u> of the  $\alpha$ -pinenyl substituents, diisopinocampheylborane only hydroborates unhindered alkenes. These reactions proceed with high enantioselectivity 2-Butene, <u>3-hexene</u> are converted to the respective chiral alcohols in high ee's. <u>Norbornene</u> under the same conditions gave an 83% ee. Heterocycle (dihydrofuran, dihydrothiophene, dihydropyrrole, tetrahydropyran) give the alcohols in  $\geq 99\%$  ee; the high ee's reflect their constrained conformations. <u>[4]</u>

It adds to alkynes to form the corresponding vinyldiisopinocampheylboranes

$$R$$
 $B = R$ 
 $G$ 
 $G = O, CR_2(R = H, C)$ 
 $H_3C$ 
 $G = O$ 

In a highly stereoselective reaction, allyldiisopinocampheylboranes converts <u>aldehydes</u> to the homologated <u>alcohols</u>, rapidly even at -100 °C. The alkyldiisopinocampheylboranes, which result from the addition to alkenes, usefully react with a range of different reagents. Hydroxylamine-O-sulfonic acid provides 3-pinanamine.

Also useful is the reaction of disopinocampheylborane with an <u>aldehyde</u> (RCHO) to give the chiral <u>boronic ester</u>, (isopinocampheyl)<sub>2</sub>BOCH<sub>2</sub>(R), which can be further used is a number of reactions e.g. Suzuki reaction. [3]

# Related campheylboranes

Treatment of diisopinocampheylborane with  $\underline{\text{TMEDA}}$  give the crystalline adduct of monoisopinocampheylborane. This adduct reacts with  $\underline{\text{boron trifluoride}}$  to liberate the monoisopinocampheylborane (IpcBH<sub>2</sub>) in 100% ee. [7] Monoisopinocampheylborane reacts with a variety of alkenes. [3] Two other reagents have been developed for the hydroboration of ketones:

In the above mechanism where G=O and R is Ipc and Cl or 9-Borabicyclononane. Diisopinocampheylchloroborane (Ipc<sub>2</sub>BCl) is produced by treating diisopinocampheylborane with <u>hydrogen chloride</u>. The chloride is reported to be more stable that the trialkyl boranes, [3] it works well with <u>aryl</u> alkyl ketones and *tert*-butyl alkyl ketones. Diisopinocampheylchloroborane is often complementary with diisopinocampheylborane, where one provides the R enantiomer and the other the S, the enantioselectivity is typically very high. [8][9]

Alpine-borane is produced by hydroborating  $\alpha$ -pinene with 9-borabicyclononane. Both of these reagents can be improved upon by using 2-ethylapopinene in place of  $\alpha$ -pinene, 2-ethylapopinene has an ethyl group in place of the methyl in  $\alpha$ -pinene. The additional steric bulk improves the stereoselectivity of the reduction.

Diisopinocampheylborane reacts with methanol to give diisopinocampheylmethoxyborane, which in turn reacts with an <u>allyl</u> or <u>crotyl</u> <u>Grignard reagent</u> to give *B*-allyldiisopinocampheylborane. This can then undergo an asymmetric allylboration to give a chiral homologated alcohol, which is a useful building block in a chiral synthesis.

# References

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Diisopinocampheylborane

Structure of (+)Diisopinocampheylborane

#### Names

Preferred IUPAC name
Bis[(1S,2S,3S,5R)-2,6,6trimethylbicyclo[3.1.1]heptan-3yl]borane

#### Other names

(+)-Di-3-pinanylborane;
Diisopinocampheylborane; lpc2BH

	Diisopinocampneyiborane; ipc2BH		
es.	Identifiers		
	CAS Number	21947-87-5	
	3D model (JSmol)	Interactive image (http s://chemapps.stolaf.ed u/jmol/jmol.php?model =%5BH%5DB%28C1 CC2CC%28C1%28 C%29%29C2%28C% 29%28C%29%29C3C C4CC%28C3%28C% 29%29C4%28C%29% 29%29C4%28C%29% 28C%29)	
	Abbreviations	Ipc <sub>2</sub> BH	
	ChemSpider	10618744 (http://www. chemspider.com/Che mical-Structure.10618 744.html)	
	PubChem CID	86278388 (https://pub chem.ncbi.nlm.nih.go v/compound/8627838 8)	
	InChI		

InChl

InChI=1S/C20H35B/c1-11-15-7-13(19(1 5,3)4)9-17(11)21-18-10-14-8-16(12 (18)2)20(14,5)6/h11-18,21H,7-10H2, 1-6H3

Key: KBGJOMVTAXYPAG-UHFFFAOY SA-N

InChI=1/C20H35B/c1-11-15-7-13(19(15, 3)4)9-17(11)21-18-10-14-8-16(12(1 8)2)20(14,5)6/h11-18,21H,7-10H2,1-6H3

Key: KBGJOMVTAXYPAG-UHFFFAOY AB

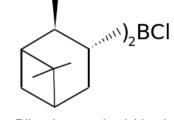
### SMILES

[H]B(C1CC2CC(C1(C))C2(C)(C))C3CC 4CC(C3(C))C4(C)(C)

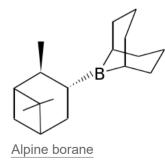
	Properties		
	Chemical formula	C <sub>20</sub> H <sub>35</sub> B	
	Molar mass	286.31 g⋅mol <sup>-1</sup>	
	Appearance	Colorless solid	

Except where otherwise noted, data are given for materials in their standard state (at 25 °C [77 °F], 100 kPa).

Infobox references



Diisopinocampheylchlorobo



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