

SYNLETT Spotlight 190

Catecholborane, a Convenient Boron Reagent

Compiled by Bangle Zhang



This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

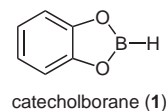
Bangle Zhang was born in Shaanxi, P. R. of China. He studied organic chemistry and obtained his B.Sc. (with honours) from Northwest University, Xi'an, P. R. of China. After having completed his M.Sc. in pharmacology at the Fourth Military Medical University, Xi'an, P. R. of China, he joined the research group of Professor Jianmin Yue. He is currently pursuing his Ph.D. in medicinal chemistry at Shanghai Institute of *Materia Medica*, Chinese Academy of Sciences, P. R. of China. His research interests include drug research and development, asymmetric catalysis and bioactive natural product synthesis.

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Introduction

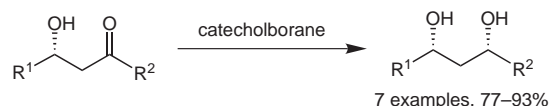
Catecholborane (**1**), known as 1,3,2-benzodioxaborole, is a versatile boron hydride reagent commercially available for synthetic organic chemistry. It is stable towards dry air and easily soluble in organic solvents. Apart from its well-known application as a new hydroborating agent in some transformations,¹ it has found a multitude of applications in reduction of various organic functional groups, organoborane-mediated cyclizations, carboxyl activation of carboxylic acids and deprotection of some functional groups. When catecholborane was associated with chiral

oxazaborolidine and chiral transition-metal-complex catalysts, a novel way to synthesize chiral alcohols in very high enantioselectivities was presented. Catecholborane can be conveniently prepared by several approaches,² and the preferred synthesis was the reaction of catechol with borane–tetrahydrofuran or borane–methyl sulfide.³



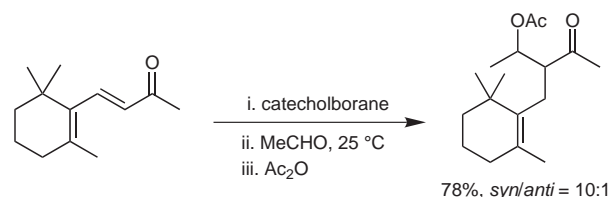
Abstracts

(A) *Stereoselective reduction of β -hydroxy ketones to syn-1,3-diols*: Evans reported a simple, mild and effective protocol for the *syn*-selective reduction of β -hydroxyl ketones using catecholborane as reducing agent.⁴ In certain instances, the stereoselectivity of the reaction could be enhanced by catalytic amounts of Rh(PPh₃)Cl.



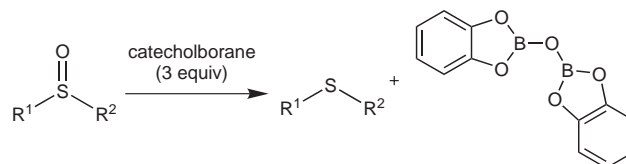
(B) *Conjugate reduction of α,β -unsaturated ketones*:

Evans also reported a conjugate reduction of α,β -unsaturated ketones by catecholborane at room temperature.⁵ The resulting intermediate boron enolates could further react with electrophiles to provide many functionalized products. Under the same conditions, other carbonyl compounds, such as α,β -unsaturated imides, esters and amides were unreactive.



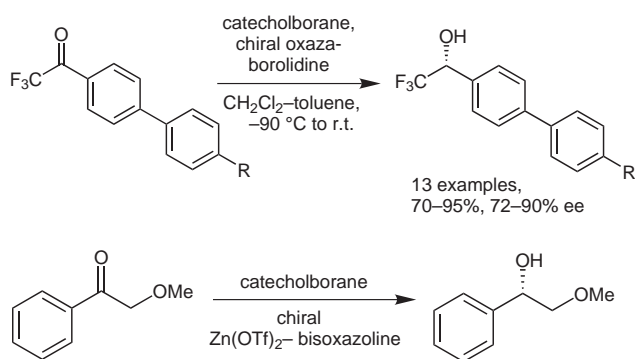
(C) *Deoxygenation of sulfoxides to sulfides*:

A gentle, efficient and selective approach for the deoxygenation of sulfoxides to the corresponding sulfides with catecholborane has been developed.⁶ Although deoxygenation of bulky or electron-withdrawing sulfoxides is slow, the reaction can be greatly accelerated with the use of excess catecholborane or by employing a rhodium catalyst.

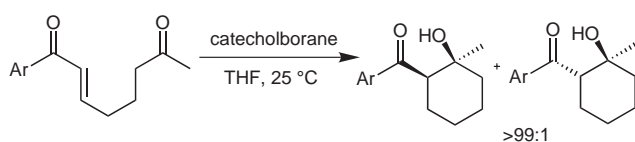


(D) Reduction of prochiral ketones to chiral alcohols:

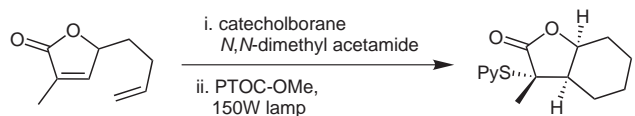
Prochiral ketones were reduced to the corresponding chiral secondary alcohols using chiral catalysts and catecholborane as stoichiometric reductant. Yields of 70–95% and ee values of 72–90% could be obtained for different (trifluoroacetyl)biphenyl derivatives when using a catalytic amount of oxazaborolidine derived from L-threonine.⁷ Enantioselective conversion of α -alkoxyketones to their corresponding α -alkoxyalcohols using $\text{Zn}(\text{OTf})_2$ -bisoxazoline complexes was also reported; this was proved to be a valuable method to afford α -alkoxyalcohols in high yields and good enantioselectivities.⁸

**(E) Aldol cycloreduction reaction mediated by catecholborane:**

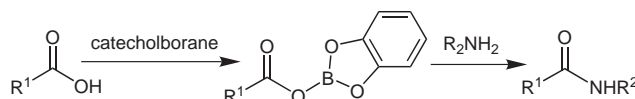
Krische and co-workers have reported the intramolecular tandem 1,4-reduction–Aldol cyclization of monoene monoketones by catecholborane.⁹ This method has been applied successfully for the construction of novel six-membered cyclic derivatives in excellent yields with high levels of *syn* diastereoselectivity.

**(F) Radical cyclization mediated by organoboranes derived from catecholborane:**

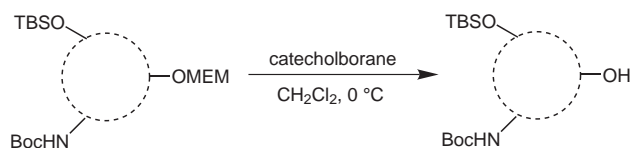
When using catecholborane as hydroboration reagent for dienes, followed by radical cyclization with pyridine-2-thione-*N*-methoxycarbonyloxy (PTOC-OMe, a Barton carbonate) as chain-transfer reagent, the bicyclic α -methylene lactone frameworks could be constructed effectively.¹⁰

**(G) Carboxyl activation for synthesis of amides and lactams:**

Collum and co-workers have reported a new and general route to amides and lactams based on acyloxyboranes, the essential carboxyl-activation intermediates, which were prepared rapidly and smoothly from carboxylic acids and catecholborane.¹¹

**(H) Deprotection of MEM ethers:**

Using catecholborane, MEM ethers could be selectively deprotected in the presence of tert-butyldimethylsilyl ethers and *N*-Boc groups.¹² This method also tolerates a wide variety of other functional groups.

**References**

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