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

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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 monoenone 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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