

SYNLETT Spotlight 202

Use of Lithiumtriethylborohydride (Superhydride) in Organic Chemistry

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

P. V. Narasimha Reddy was born in Mahaboobnagar, Andhra Pradesh state in India in 1978. He obtained his B. Sc. (1999) from Osmania University and Masters Degree (2002) in Chemistry from the University of Hyderabad. He qualified for the CSIR fellowship through a National Search Exam. After qualifying for CSIR-JRF, as a graduate student, he started working towards his Ph.D. under the supervision of Dr. P. Radha Krishna at Indian Institute of Chemical Technology, Hyderabad, India. Currently, he is a fourth-year Ph.D. student. His research interests are synthesis of biologically active natural products by using asymmetric synthesis/Chiron approach, developing synthetic methodologies, asymmetric Baylis–Hillman reaction and its applications.

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Introduction

Lithiumtriethylborohydride (LiEt_3BH) was used as versatile reagent in organic chemistry for various chemical transformations including reduction of carbonyl compounds, including selective reductions, in the regioselective ring-opening reactions, in deoxygenation reactions and as an *N*-acyl deprotecting agent.

*Preparation of lithiumtriethylborohydride (LiEt_3BH) in THF:*¹

Solutions of lithiumtriethylborohydride (LiEt_3BH) in THF were conveniently prepared by stirring 1 equiv of triethylborane with an excess of finely divided lithium-hydride (usually in moderate excess) in THF for approximately 24 h at 25 °C, followed by refluxing for 2–3 h.

Filtration removed the excess lithium hydride and gave a clear solution. The concentration was determined by hydrolyzing an aliquot of the solution with a water/glycerin/THF (1:1:1) mixture at 25 °C and measuring the hydrogen evolved. The yields were quantitative (Equation 1).

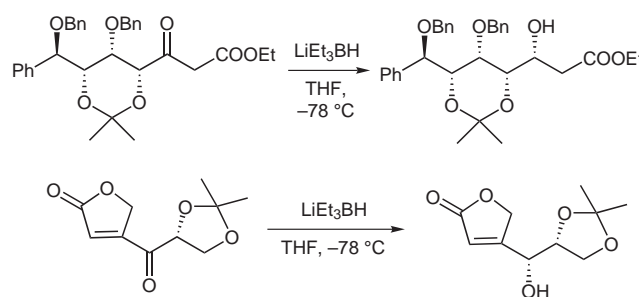


Equation 1

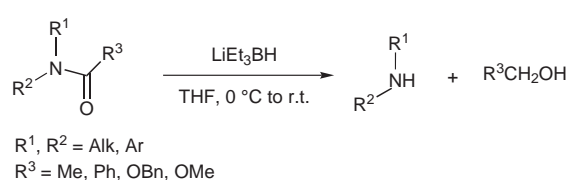
Under an inert atmosphere, solutions of lithiumtriethylborohydride (LiEt_3BH) in THF appear to be stable indefinitely with no change observed in months at room temperature and in days at 65 °C.

Abstracts

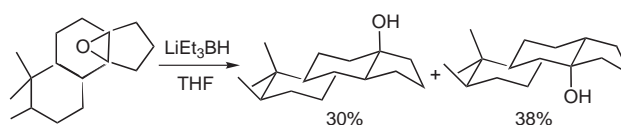
(A) 1,2-*Syn* stereoselective reduction of α -hydroxy carbonyl compounds in very good diastereomeric excess can be achieved by using lithiumtriethylborohydride.^{2,3}



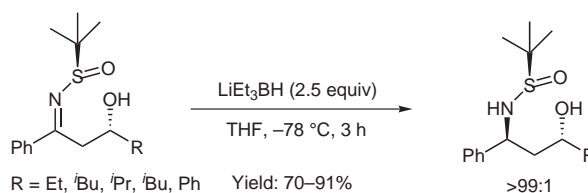
(B) Selective *N*-acyl deprotection can be performed using LiEt_3BH agent under mild reaction conditions while other groups such as ethers are unaffected.⁴



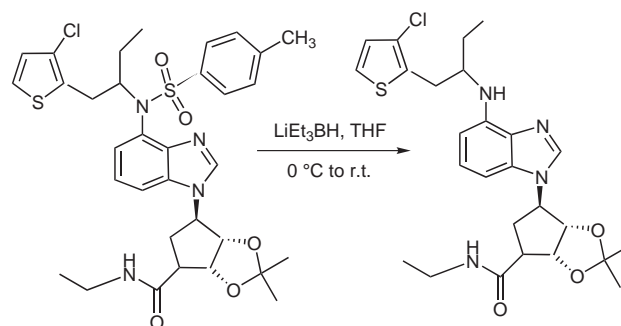
(C) Regioselective reductive opening of the epoxide with lithiumtriethylborohydride can be performed with moderate selectivity.⁵



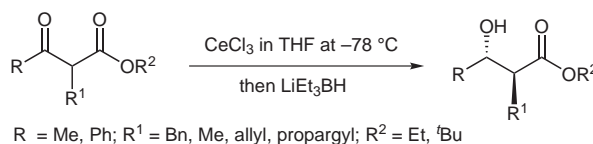
(D) Highly diastereoselective reduction of α -hydroxy-*N*-sulfinyl imines to the corresponding secondary amines can be achieved.⁶



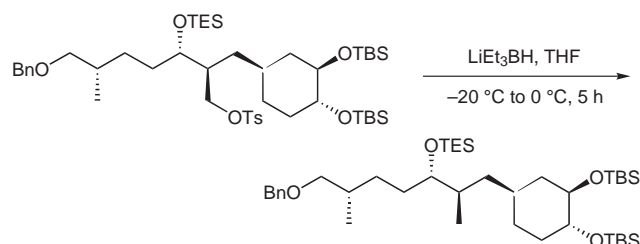
(E) Lithiumtriethylborohydride can be used in the selective deprotection of *N*-toluene sulfonyl protecting group to give corresponding amines.⁷



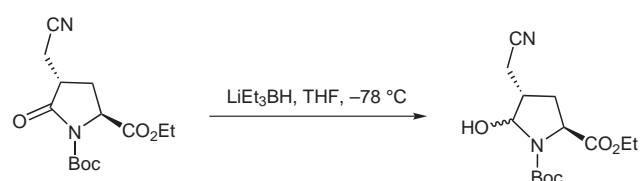
(F) Efficient diastereoselective synthesis of threo- α -alkyl- β -hydroxy esters is conveniently possible by the reduction of α -alkyl- β -keto esters with $\text{LiEt}_3\text{BH}/\text{CeCl}_3$.⁸



(G) LiEt_3BH can be used in the selective deoxygenation reactions when the hydroxyl functional groups are protected as their tosylates without affecting other protecting groups.⁹



(H) LiEt_3BH can be efficiently utilized for the reduction of the highly functionalized *N*-Boc-protected lactams in THF at -78°C to their corresponding pyrrolidin-2-ols without affecting the other functionalities.¹⁰



References

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