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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

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Lithium Amino Borohydrides (LABs)

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Introduction

Lithium amino borohydride reagents (LABs) are a new class of powerful and selective reagents that were first introduced by Singaram et al. in 1992. The reactivity of these reagents is comparable to lithium aluminium hydride. However, they have several advantages over lithium aluminium hydride, e.g., they are air-stable, non-pyrophoric, thermally stable and hydrolyse only slowly in protic solvents above pH 4. Thus LABs can perform in air virtually all of the transformations for which LAH is commonly used and offer significant advantages in safety, selectivity, and ease of handling and simple work-up

procedures. In short, LAB is an attractive alternative to LAH or super hydride reduction.

LABs can be prepared as solids or 1–2 M THF solutions, or they can be generated in situ for immediate use by the reaction of *n*-BuLi or MeLi with amine–borane complexes to the corresponding LABs. LABs can be prepared from any primary or secondary amine, thus allowing precise steric and electronic control of their reactivity by modulation of the substituents on the nitrogen atom.

In 1995, Kagan and co-workers reported the only chiral LAB reagent. However, the reduction of ketones using this reagent afforded the corresponding alcohols in low ee (5–9%).²

Abstracts

(A) The LAB reagents are capable of reducing a wide range of functional groups, which are summarized in the following scheme.^{1d}

(B) In addition to hydride transfer, LABs can transfer the amine moiety. Under mild reaction conditions, they promote the amination of 2-halopyridine (X = F, Cl, Br), providing the 2-(dialkylamino)pyridines in excellent yield and purity.³

$$\begin{array}{c} LiBH_3NR_2 \\ \hline N & X \end{array}$$

$$X = F, Cl, Br$$

$$N = R_2$$

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(C) The ability of LAB reagents to function as both reducing agent and amination reagent allows the performance of tandem amination–reduction reactions.⁴

(D) Braslau et al. reported chemoselective reduction of esters using LAB to afford the corresponding *N*-alkoxyamine alcohols, which are used as initiators in 'living' free radical polymerizations.⁵

(E) LAB is now widely used for the removal of Evan's chiral auxiliary and reduction of amides to the corresponding alcohols. Theodorakis and co-workers employed this reaction to reduce an amide to the corresponding alcohol in the total synthesis of borelledin.⁶

(F) Sessler et al. reported the synthesis of a new set of dipyrrolylpyrazines utilizing lithium pyrrolidino borohydride. Pyrazine oligomers are anion receptors for various biologically important anions.⁷

(G) At low temperature, LABs react with halides to afford the corresponding amines.⁸ Lodeiro and co-workers extended this chemistry to the synthesis of a new photoinduced electron-transfer (PET) system.⁹

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