Sodium Bis(methoxyethoxy)-
aluminium Hydride

Compiled by Akshat Rathi

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Introduction

Sodium bis(methoxyethoxy)aluminium hydride (Red-Al®) is a versatile reducing agent which was developed by Vit and co-workers in 1968.1

Red-Al® exhibits similar reactivity to lithium aluminium hydride but is significantly less sensitive towards air and has higher solubility in aromatic solvents and ethers. In addition, the reactions can be performed at temperatures of up to 200 °C.2 The general mechanism of reduction using Red-Al® involves an initial reaction with an alcohol, formation of hydrogen, and subsequent hydride transfer in an intramolecular fashion. In the absence of such a moiety, the hydride reduction via a mechanism akin to lithium aluminium hydride can be envisaged. The reagent has been used towards the synthesis of many natural products.3 Some less conventional uses involve the cleavage of benzyl ethers of vicinal methoxy-containing compounds.4

Abstracts

(A) Koide et al. reported the use of NaBH4 or Red-Al® to achieve the reduction of propargylic alcohols to allylic alcohols. They demonstrated that Red-Al® gave only E alkenes whereas NaBH4 gave E/Z mixtures. Superior yields were obtained with Red-Al® compared to NaBH4 and fewer equivalents were required. It has also been shown that the metalated intermediates can be intercepted by an electrophile, thus allowing derivatization of the alkenes in a single operation.5

(B) Igawa and Tomooka reported the regioselective reduction of a bisalkyne to an E alken. Following the preferential order of reactivity TPS > Ph ~ TBDPS > TIPS ~ TMS >> Alk, Red-Al gave regioselectivities from 72:28 to 97:3 and 79–100% yields. Other hydride reagents were reported to be less selective than Red-Al®.6

(C) Shibasaki et al. recently reported the use of Red-Al® in the reduction of α,β-epoxy peroxy esters to aldehydes in high yields. In this interesting transformation, the reduction of such an ester could be achieved without epoxide opening.7

(D) En route to the synthesis of dicyclopenta[α,ε]pentalenes, Cao et al. successfully utilized Red-Al® in the reduction of a tetrayne to the corresponding bisallene–bisalkyne under high dilution conditions. Several reducing reagents including LiAlH4 proved unsuccessful prior to achieving satisfactory results with Red-Al®. The reduction presumably occurs by formation of an aluminium complex of the propargylic alcohol and subsequent delivery of hydride in an S_N2′ fashion.8
References