



Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Tetrahedron report XXX

Applications of sodium borohydride procedure for the reductive removal of Evans and other chiral auxiliaries

Mahavir Prashad*, Wen-Chung Shieh, Yugang Liu

Chemical & Analytical Development, Novartis Pharmaceuticals Corporation, East Hanover, NJ 07936, USA

ARTICLE INFO

Article history:

Received 9 July 2015

Available online xxx

Keywords:

Evans adol reaction
 Evans chiral auxiliary
 Prashad method
 Reductive removal
 Sodium borohydride

Contents

1.	Introduction	00
2.	Natural products synthesis	00
2.1.	Asymmetric aldol reaction and removal of auxiliary	00
2.1.1.	Reveromycin B synthesis	00
2.1.2.	Cassaine synthesis	00
2.1.3.	Formamicin synthesis	00
2.1.4.	Pectenotoxin-2 synthesis	00
2.1.5.	(–)-Lasonolide A synthesis	00
2.1.6.	(–)-Brevenal synthesis	00
2.1.7.	Tedanolide synthesis	00
2.1.8.	Gambieric acid synthesis	00
2.1.9.	Bitungolides A-E synthesis	00
2.1.10.	(–)-Bitungollide F synthesis	00
2.1.11.	Pamamycin 621A synthesis	00
2.1.12.	Rhizopodin synthesis	00
2.1.13.	Yaku'amide A synthesis	00
2.1.14.	Didemnaketal B synthesis	00
2.1.15.	Nonactin synthesis	00
2.2.	Asymmetric alkylation and removal of auxiliary	00
2.2.1.	(–)-Isolaurallene synthesis	00
2.2.2.	(–)-Laulimalide synthesis	00
2.2.3.	(+)-Neopeltolide synthesis	00
2.2.4.	(+)-Vittatalactone synthesis	00
2.2.5.	(+)-Spongidepsin synthesis	00
2.2.6.	Phenylpropanoids synthesis	00

* Corresponding author. E-mail address: mahavir.prashad@novartis.com (M. Prashad).

2.2.7.	(–)-Calyciphylline synthesis	00
2.2.8.	Leucascandrolide A synthesis	00
2.3.	Asymmetric Michael addition and removal of auxiliary	00
2.3.1.	(+)-Vinblastine synthesis	00
2.3.2.	Apratoxin A synthesis	00
2.3.3.	(+)-Hamacanthins synthesis	00
2.3.4.	(–)-Virgatusin and (+)-urinaligran synthesis	00
2.4.	α -Hydroxylation and removal of auxiliary	00
2.4.1.	Palmerolide A synthesis	00
3.	Synthesis of drug candidates	00
3.1.	Synthesis of ^{14}C -labeled and tritiated LY450108	00
3.2.	Synthesis of PNP405	00
3.3.	Synthesis of 2R,2'R-methylphenidate	00
4.	Liquid crystal synthesis	00
4.1.	Synthesis of chiral liquid crystals	00
5.	Reductive removal of other auxiliaries and heterocyclic amides	00
5.1.	(+)-Brefeldin A synthesis	00
5.2.	Sanglifehrin A synthesis	00
5.3.	Erogorgiaene synthesis	00
5.4.	Asymmetric aldol additions with a titanium enolate of <i>N</i> -thioglycolyl oxazolidinethione	00
5.5.	Synthesis of chiral γ -aryl-1 <i>H</i> -1,2,4-triazoles	00
5.6.	Synthesis of β -mercapto alcohol	00
5.7.	1,3-Dipolar cycloadditions of nitrones	00
5.8.	1,3-Dipolar cycloadditions of nitrile oxides	00
5.9.	Rearrangement of 5-phenylthiazolidine-2,4-diones	00
6.	Resin-bound auxiliaries	00
6.1.	Polymer-bound auxiliaries	00
7.	Other applications: synthetic methodologies	00
7.1.	Diastereoselective alkylations of oxazolidinone glycolates	00
7.2.	Diastereoselective alkylations of oxazolidinone vinylogous glycolates	00
7.3.	Stereochemical control on the Michael addition	00
7.4.	Michael reactions of titanium enolates of glycolic acid derivatives with morpholine amides of acrylic acid	00
7.5.	Enantioselective Mannich-type reaction	00
7.6.	Construction of C–S bonds with a quaternary stereocenter	00
8.	Limitations	00
8.1.	Synthesis of Δ^3 -2-hydroxybakuchiol, bakuchiol and ent-bakuchiol	00
8.2.	(+)-Discodermolide synthesis	00
9.	Summary	00
	References and notes	00
	Biographical sketch	00

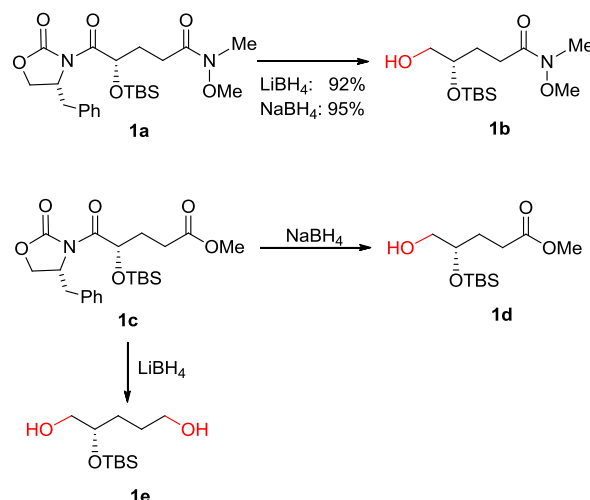
1. Introduction

In early eighties, Evans and his co-workers developed chiral 2-oxazolidinones as efficient auxiliaries for asymmetric synthesis. Since then, it has been demonstrated that employing this class of chiral auxiliary, high diastereoselectivity can be achieved in reactions such as aldol reactions, alkylations, brominations, conjugate additions, cycloadditions, Diels–Alder reactions, hydroxylations, and Michael additions.^{1–5}

Several methodologies were developed to remove these auxiliaries, after attaining the desired asymmetric induction, based on the functionalities needed for the subsequent chemical transformations: reduction (LiAlH_4 , LiBH_4 , NaBH_4) to alcohol, hydrolysis (LiOH , H_2O_2) to carboxylic acid, methanolysis (NaOMe , MeOH) to ester, and transamination (MeONHMe , Me_3Al) to Weinreb amide.⁵ For reductive removal of these auxiliaries, LiAlH_4 and LiBH_4 were developed initially.^{6–8} A more economical, practical and racemization-free method for the reductive removal of 2-oxazolidinones with NaBH_4 in a mixture of THF and water was later reported by Prashad et al.⁹

Lithium aluminum hydride is useful for molecules containing no functional groups that are vulnerable to reduction, such as esters. Lithium and sodium borohydride have been extensively used. In one study, reductive removal of oxazolidinone auxiliary of **1a** with LiBH_4 or NaBH_4 gave similar results when compared side by side

(Scheme 1).¹⁰ However, reduction of **1c** with LiBH_4 led mainly to diol **1e** (both the oxazolidinone and the ester were reduced). In contrast, reductive removal of oxazolidinone auxiliary of **1c** with NaBH_4 was chemoselective affording only product **1d**.¹⁰



Scheme 1.

Download English Version:

<https://daneshyari.com/en/article/5213957>

Download Persian Version:

<https://daneshyari.com/article/5213957>

[Daneshyari.com](https://daneshyari.com)