Triethylborane (Et₃B)

Gavin O’Mahony

Gavin O’Mahony was born in Donegal, Ireland in 1980 and began studying chemistry at Queen’s University Belfast in 1997. After receiving his B.Sc. in 2000, he joined the research group of Dr Paul J. Stevenson at Queen’s and is currently undertaking a Ph.D. project in conjunction with CSS Ltd. as part of the CAST Award Scheme. His research is in palladium and ruthenium catalysed approaches to pumiliotoxin alkaloids.

School of Chemistry, Queen’s University of Belfast, David Keir Building, Stranmillis Road, Belfast, BT9 5FS, Northern Ireland, UK

Introduction

Triethylborane is a colourless liquid that is spontaneously flammable in air, burning with a characteristic green flame. It is readily autoxidised by molecular oxygen via a radical mechanism (Scheme 1).

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\begin{align*}
\text{Initiation:} & & \text{Et₃B} + O₂ & \rightarrow & \text{Et₃BOO}^* + \text{Et}^* \\
\text{Propagation:} & & \text{Et}^* + O₂ & \rightarrow & \text{EtOC}^* \\
& & \text{EtOC}^* + \text{Et₃B} & \rightarrow & (\text{EtOO})\text{BEt}_3 + \text{Et}^*
\end{align*}
\]

Scheme 1

This reactivity of triethylborane leads to one of its most common applications, i.e. as an initiator in radical reactions.

The first use of triethylborane as a radical initiator was reported in 1989 by Oshima. Its main advantage is its effectiveness at low temperature (–78 °C), which is useful in the case of stereoselective radical reactions or with thermally unstable reaction products. The use of AIBN, which forms radicals by thermal decomposition, is clearly not feasible in these cases, making triethylborane an attractive alternative. The use of organoboranes as a source of radicals has been recently reviewed.

Abstracts

(A) Sibi and co-workers used triethylborane as the radical initiator in their enantioselective syntheses of butyrolactone natural products. Lewis-acid mediated radical addition to differentially protected fumarate 1 gave addition product 2 in 80% yield as a single diastereoisomer. This was further elaborated to afford the dibenzylbutyrolactone lignan (–)-arctigenin. Similar chemistry was used to synthesise the butyrolactone natural products (–)-enterolactone, (–)-isoeartigenin, (–)-nephrosteranic acid and (–)-roccellaric acid.

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Malacria and co-workers used triethylborane/O2 as the radical initiator in their tin-free method for the intramolecular addition of alkyl radicals to aldehydes and ketones. Efficient cyclisation of 3-iodoaldehydes was accomplished with 10 equivalents of triethylborane. 3-Iodoketones required 20 equivalents of triethylborane to ensure a good yield of the desired product. The use of triethylborane as a radical initiator reverses the selectivity observed in the cyclisation of enal precursors with AIBN/Bu3SnH, with cyclisation onto the carbonyl carbon preferred with triethylborane. This is attributed to the Lewis acidity of the borane.

Triethylborane has been used in the radical hydroindation of alkenes and alkynes. Alkenylindiums generated by this means can be employed in a one-pot cross-coupling with aryl halides or trapped with various electrophiles. The hydroindation of alkynes and subsequent palladium-catalysed cross-coupling proceeds with high (Z)-selectivity. The (Z)-alkenylindiums thus formed can also be trapped with various electrophiles, such as water and I2, with retention of the alkenylindium stereochemistry. Hydrogallation proceeds with lower (Z)-selectivity.

Chandrasekhar and co-workers reported the first non-metal mediated tandem Michael-aldol reaction for the synthesis of α-alkyl-β-hydroxy ketone derivatives using triethylborane.

Tamaru and co-workers have used triethylborane as an efficient promoter of the palladium-catalysed alkylation of active methylene compounds with unactivated aliphatic alcohols. The primary role of the borane is to activate the C–O bond of the allylic alcohol towards oxidative addition by the Pd2+ species.

Chandrasekhar and co-workers reported the first non-metal mediated tandem Michael-aldol reaction for the synthesis of α-alkyl-β-hydroxy ketone derivatives using triethylborane.

Tomiioka and co-workers have investigated the initiator-dependent chemoselective addition of THF radical to aldehydes and imines in a three component reaction. Triethylborane preferentially afforded the THF adduct of the aldehyde. The use of dimethylzinc as initiator preferentially gave the THF adduct of the corresponding imine. The reason for this chemoselectivity is not explained.

References