SYNLETT
Spotlight 426

Bis(pinacolato)diboron
Compiled by Rémy Hemelaere

Rémy Hemelaere was born in 1987 in Menin, Belgium. He graduated from National Polytechnic School of Chemical Engineering and Technology of Caen (Ensicaen, France) in 2010 and received his M.Sc. degree in organic chemistry in the same year. He is currently pursuing his Ph.D. under the supervision of Dr. François Carreaux at the University of Rennes 1, France. His Ph.D. research project focuses on allylboronate chemistry and the utilisation of ruthenium metathesis catalysts. He is developing methodologies for the total synthesis of natural molecules.

Université de Rennes 1 – Institut des Sciences Chimiques de Rennes – UMR CNRS 6226, 263 Avenue du Général Leclerc, Campus de Beaulieu - Bâtiment 10B, 35042 Rennes, France
E-mail: remy.hemelaere@univ-rennes1.fr

Introduction

Bis(pinacolato)diboron (B₂pin₂, Figure 1, CAS: 73183-34-3) is an air-stable, odourless, colorless powder that is commercially available. Being a major tool for the introduction of boron atoms into organic compounds, it is widely known as a good reagent to prepare substrates for the Suzuki–Miyaura reaction.

An extensive scope of reactions, including C–H activation of C(sp²)–H and C(sp³)–H bonds, borylation of α,β-unsaturated derivatives and substitutions of allylic carbonates, have been recently described in the literature. Over the past few years, extensive efforts have been devoted to the borylation of dienes, allenes, alkynes.

Borylated products, obtained from these new strategies, could successfully be used in oxidation, allylation or coupling reactions.

Abstracts

(A) C(sp³)–H Activation
Very recently, Sawamura et al. reported a rhodium-catalyzed C(sp³)–H borylation of amides and urea derivatives at the position adjacent to nitrogen with a silica-supported triarylphosphine ligand (silica-TRIP). The reaction was carried out under mild conditions with good to excellent yield. Compounds obtained with this method can undergo Suzuki–Miyaura coupling.

(B) Allylic Substitution
Under mild conditions, allylic carbonates can be borylated by treatment with bis(pinacolato)diboron in the presence of a copper catalyst to give the corresponding allyl boronates. Using a chiral ligand, excellent enantioselectivities were obtained.

(C) Borylation of Aldehydes
Treatment of aldehydes with B₂pin₂ in the presence of a copper catalyst, led to the formation of diboration products as stable compounds in the solid state. A mechanistic study was performed confirming the insertion of the carbonyl group into the copper–boron bond. A selective hydrolysis of the B–O bond during chromatographic purification can provide the corresponding α-hydroxyboronates.

SYNLETT 2013, 24, 0659–0660
Advanced online publication: 12.02.2013
© Georg Thieme Verlag Stuttgart · New York
Over the past eight years, research has focused on boron-substituted quaternary carbons. Starting from primary alkyl bromides, Biscoe et al. reported the synthesis of α,β-unsaturated esters, amides, and ketones. These processes are efficiently catalyzed by N-heterocyclic carbene (NHC) complexes of copper(I). Hoveyda’s group applied this strategy to trisubstituted α-unsaturated esters. With a chiral NHC-copper complex, they developed an enantioselective pathway to boron-substituted quaternary carbons.

References