

SYNLETT Spotlight 89

Synthetic Applications of Tris(pentafluorophenyl)borane

Compiled by Robert B. Kargbo



This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

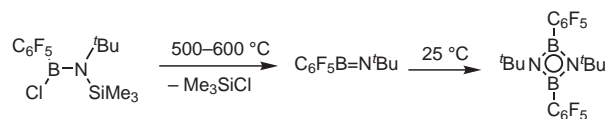
Robert B. Kargbo was born in Freetown, Sierra Leone, and he completed his Bachelor degree in Chemistry at Fourah Bay College in Freetown. He fled war-torn Sierra Leone in 1997 and settled in North Dakota, USA, where he is presently pursuing his PhD under the guidance of Dr. Gregory R. Cook. His research interest is focused on palladium catalyzed-indium mediated allylation reactions.

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Introduction

Reactions in the presence of Lewis acids are commonplace in modern synthetic chemistry.¹ Pentafluorophenylborane compounds were first reported in the 1960s by Chambers² and Massey but their strong Lewis acidity was unexploited until the 1980s when Paetzold and co-workers generated monomeric iminoborane which undergoes cycloaddition reactions with nitriles or isonitriles (Equation 1).³ Since then, their application in catalysis has increased tremendously.⁴ Tris(pentafluorophenyl)borane has emerged as a powerful but selective reagent in many organic transformations.⁵ Due to its uniqueness, it is a ubiquitous component of many important alkyl-based olefin polymerization catalysts and functions in non-traditional Lewis acid catalyzed reactions involving reduction

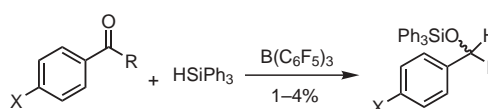
of alcohols, cleavage of aryl and alkyl ethers, nonactivated aziridines⁶ and epoxides. Furthermore, it catalyzes hydrosilylation of aromatic aldehydes, ketones, ethers,⁷ and imines.⁸ Tris(pentafluorophenyl)borane is commercially available but various methods have been developed over the years for its preparation. One preparation involves the formation of a pentafluorophenyl metal (Group 11 or 12), followed by treatment with a boronhalide.⁹



Equation 1

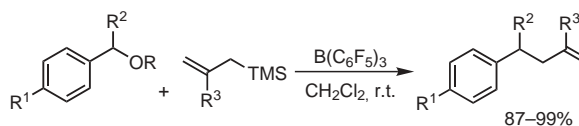
Abstracts

(A) Hydrosilylation of aromatic compounds catalyzed by 1–4 mol% of tris(pentafluorophenyl)borane is a mild and selective addition of Ph_3SiH at room temperature. Yields and conversion rates for this transformation are high and the reactivity order is esters \gg ketone $>$ aldehyde which is paradoxical to the normal reactivity pattern.⁸

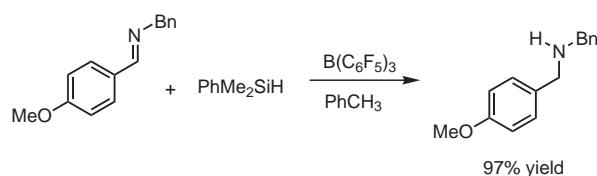


X	R	Rate	Yield (%)
H	OEt	Very fast	80
NO_2	Me	Fast	91
NO_2	H	Slow	96

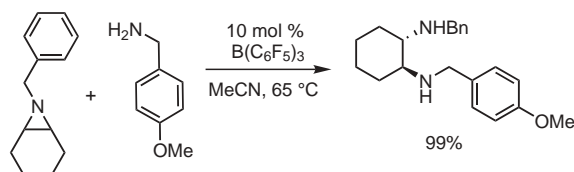
(B) Secondary benzylic alcohol derivatives undergo allylation with allylsilanes in the presence of catalytic amounts of $\text{B}(\text{C}_6\text{F}_5)_3$. Other functionalities such as bromo, acetoxy, and primary benzyloxy groups also undergo smooth allylation.¹⁰



(C) Reduction of imines to amines is an important organic transformation. A variety of benzaldimines and ketimines are mildly and effectively hydrosilated in good to excellent yields.¹¹



(D) Aziridine ring opening is an important organic transformation that generates versatile nitrogen building blocks found in many biological systems. Nonactivated aziridines undergo nucleophilic ring opening with catalytic amounts of $B(C_6F_5)_3$ to yield the corresponding *trans*-diamine.⁶



References

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