

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

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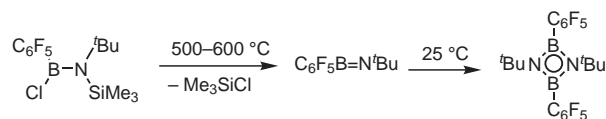
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Introduction

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

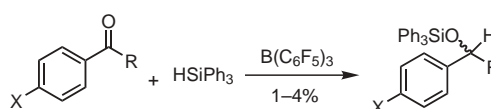
of alcohols, cleavage of aryl and alkyl ethers, nonactivated aziridines⁶ and epoxides. Furthermore, it catalyzes hydrosilylation of aromatic aldehydes, ketones, ethers,⁷ and imines.⁸ Tris(pentafluorophenyl)borane is commercially available but various methods have been developed over the years for its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



Equation 1

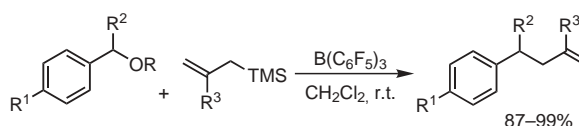
Abstracts

(A) Hydrosilation 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 >> ketone > aldehyde which is paradoxical to the normal reactivity pattern.⁸

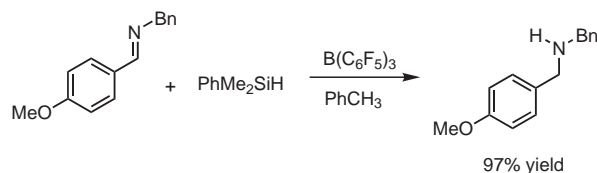


X	R	Rate	Yield (%)
H	OEt	Very fast	80
NO ₂	Me	Fast	91
NO ₂	H	Slow	96

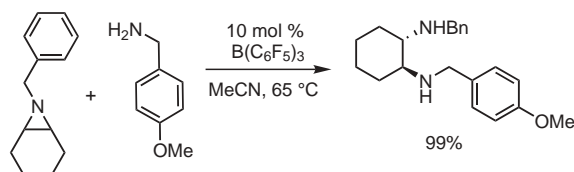
(B) Secondary benzylic alcohol derivatives undergo allylation with allylsilanes in the presence of catalytic amounts of $\text{B(C}_6\text{F}_5)_3$. Other functionalities such as bromo, acetoxy, and primary benzyloxy groups also undergo smooth allylation.¹⁰



(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 $\text{B}(\text{C}_6\text{F}_5)_3$ to yield the corresponding *trans*-diamine.⁶



References

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