SYNLETT Spotlight 89

Synthetic Applications of Tris(pentafluorophenyl)borane

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

References

- (1) (a) Mahrwald, R. *Chem. Rev.* **1999**, 99, 1095. (b) Sibi, M. P.; Rheault, T. R. *J. Am. Chem. Soc.* **2000**, 122, 8873.
- (2) Chambers, R. D.; Chivers, T. J. *Organomet. Chem. Rev.* **1966**, 5, 279.
- (3) Piers, W. E.; Chivers, T. *Chem. Soc. Rev.* **1997**, 26, 345.
- (4) (a) Ishihara, K.; Funahashi, M.; Hanaki, N.; Miyata, M.; Yamamoto, H. *Synlett* **1994**, 963. (b) Ishihara, K.; Hanaki, N.; Yamamoto, H. *Synlett* **1993**, 577.
- (5) Chen, E. Y.-X.; Marks, T. J. *Chem. Rev.* **2000**, 100, 1391.
- (6) Watson, I. D. G.; Yudin, A. K. *J. Org. Chem.* **2003**, 68, 5160.
- (7) Piers, W. E.; Parks, D. J. *J. Am. Chem. Soc.* **1996**, 118, 9440.
- (8) Blackwell, J. M.; Sonmor, E. R.; Scoccitti, T.; Piers, W. E. *Org. Lett.* **2000**, 2, 3921.
- (9) Preparation of tris(pentafluorophenyl)borane: Wilson, D. R.; Lapointe, R. E. Dow Chemical Company, USA, U.S. Patent 5744646, **1998**.
- (10) Gevorgyan, V.; Rubin, M. *Org. Lett.* **2001**, 3, 2705.
- (11) Blackwell, J. M.; Piers, W. E.; Parvez, M. *Org. Lett.* **2000**, 2, 695.