

SYNLETT Spotlight 266

Organotrifluoroborate Salts

Compiled by Roberta A. Oliveira



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

Roberta A. Oliveira was born in Recife, Brazil in 1980. She studied chemistry at the Federal University of Pernambuco, Brazil. At the same University, she started her Ph.D studies in May, 2006, working on the development of new methods based on organometallic reagents. Because her advisor in Brazil, Prof. Paulo H. Menezes, has a research collaboration with Prof. Gary A. Molander from the University of Pennsylvania, she started a new project with Dr. Molander in green synthetic methods involving organotrifluoroborates. Her research is focused on the application of organotrifluoroborate methods to the synthesis of natural products analogues.

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Introduction

Organotrifluoroborate salts are a unique class of organoboron compounds that have emerged as promising synthetic reagents. The tetracoordinate nature of the boron in these complexes, enhanced by strong boron-fluorine bonds, was anticipated to prevent undesired typical reactions of trivalent organoborons. This, in turn, would make the organotrifluoroborates essentially a protected boronic acid or boronate ester reagents.¹

The most convenient method for the preparation of these compounds from boronic acids and derivatives utilizing the readily available and inexpensive KHF_2 was described

by Vedejs and co-workers.² In combination with this process, potassium organotrifluoroborates can be readily prepared by the transmetalation of organolithium or organomagnesium reagents with trialkylborates.³ Alternatively, they can be synthesized by various catalyzed or uncatalyzed hydroborations of alkynes or alkenes.⁴

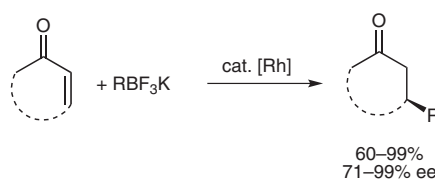
The utilization of organotrifluoroborates in organic synthesis led to the preparation of more functionalized compounds. In this way, several functional group interconversion reactions have been performed,⁵ which expands the range of retrosynthetic pathways using organotrifluoroborates as key intermediates in complex molecule synthesis.

Abstracts

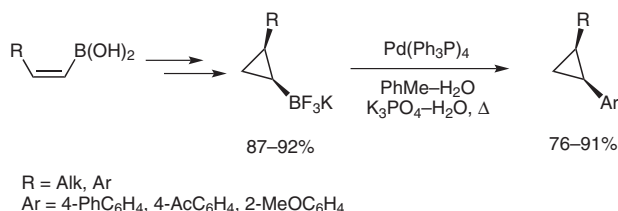
(A) The cross-coupling reaction of potassium aryltrifluoroborates with arenediazonium salts⁶ can be performed at low temperatures and in absence of a base. However, the cross-coupling reaction of aryl-, alken-1-yl, alkyl-, allyl-, and alky-1-yltrifluoroborates with aryl halides or triflates requires the addition of a base to proceed.⁷



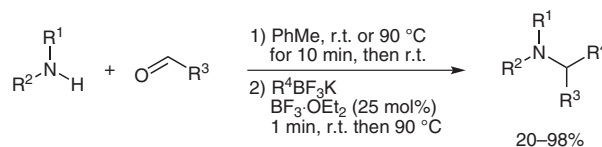
(B) Several chiral rhodium(I) complexes promoted efficiently the conjugated addition of potassium alkenyl- and aryl-trifluoroborates to α,β -unsaturated ketones to give the corresponding Michael adducts in good yields and enantiomeric excesses.⁸



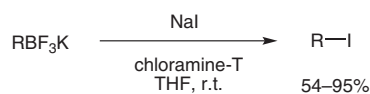
(C) Enantiomerically pure cyclopropanes can be obtained in high yields from Suzuki–Miyaura cross-coupling reactions of potassium cyclopropyltrifluoroborates and aryl bromides with retention of the configuration.⁹



(D) Raepfel and co-workers developed a three-component Lewis acid-catalyzed Mannich-type reaction using potassium organotrifluoroborates (aryl, vinyl, and allyl reagents) as an extension of the standard Pétasis reaction.¹⁰

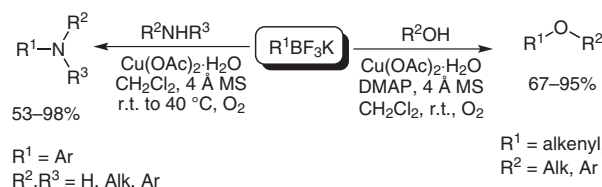


(E) Aryl-, heteroaryl-, alkenyl- and alkynyltrifluoroborates are rapidly converted into the corresponding iodides under mild conditions using sodium iodide in the presence of chloramine-T. The reaction is stereospecific and proceeds in moderate to excellent yields.¹¹

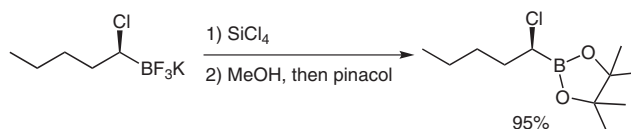


R = Ar, Hetero, alkenyl, alkynyl

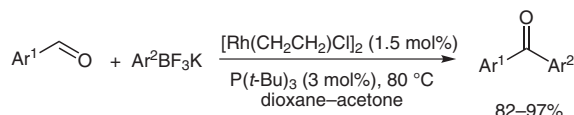
(F) The cross-coupling of alcohols and amines with potassium organotrifluoroborates catalyzed by copper(II) under mild and essentially neutral conditions gave the corresponding ethers and amines in moderate to good yields. A broad range of functional groups are tolerated on both of the cross-coupling partners.¹²



(G) Potassium organotrifluoroborates can also be useful precursors of boronic esters via the intermediate formation of dihalogenoborane.¹³



(H) The cross-coupling reaction of potassium organotrifluoroborates and aldehydes to access ketones under mild conditions via a Heck-type mechanism gave the corresponding ketones in good yields.¹⁴



References

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