

SYNLETT Spotlight 20

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

Pinacolborane

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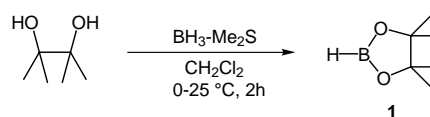
Yi-Lin Song studied chemistry at Nanjing University, then received his Ph.D. in asymmetric synthesis using organoborons from the University of Fudan in Shanghai (1999). He is currently working as a post-doctoral fellow with Ch. Morin studying the preparation of boronated analogues of biomolecules.



Pinacolborane **1** is a hydroboration reagent that offers several advantages over catecholborane: milder reaction conditions, higher functional group tolerance, and better regio- and stereo-selectivity. Compound **1** can be used for the direct introduction of boronates by its reaction with alkenes, alkynes, or aryl halides. The resulting pinacolboronates, which display excellent aqueous and chromatographic stability, can be further used in C-C bond forming reactions, such as Suzuki-Miyaura couplings.

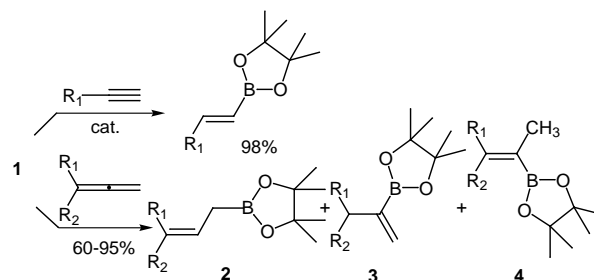
Preparation:¹ Pinacolborane **1** is easily prepared: 1 equiv of borane-dimethyl sulfide (10 M solution in Me₂S) was

added to a solution of redistilled pinacol in dry dichloromethane at 4 °C, which is then stirred for 1 h. The solution was allowed to warm to 25 °C and stirring was continued until gas evolution was complete (usually 1 h). This solution is ready for use for most applications. If desired, >99% pure pinacolborane can be isolated as a clear liquid by distillation (bp = 42-3 °C/50 mm Hg).

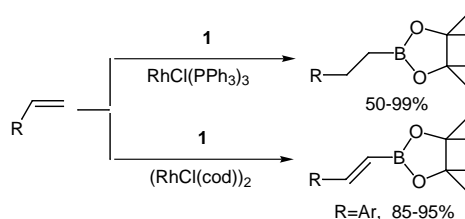


Abstracts

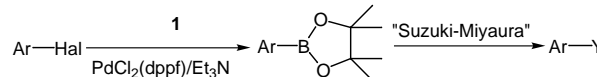
(A) Compound **1** can perform hydroboration of alkynes,¹ catalyzed by transition metals (Rh, Ni), to give vinylboronates in essentially quantitative yield.² The regioselectivity of hydroboration of allenes under Pd(0) catalysis can be fully controlled (to give **2**, **3**, or **4**) by varying the phosphine ligands.³



(B) Rh-catalyzed hydroboration of alkenes or vinylarenes gives the corresponding pinacolboronates;² when phosphines are not catalyst ligands, the dehydrogenative borylation of aryl alkenes proceeds predominantly.⁴



(C) Compound **1** can also couple with aryl halides.⁵ The arylboronates thus obtained can then be used in Suzuki-Miyaura coupling reactions, as shown by the enantioselective synthesis of 4-substituted phenylalanines.⁶



References and Notes

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