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A Sydnone Cycloaddition Route to Pyrazole Boronic Esters
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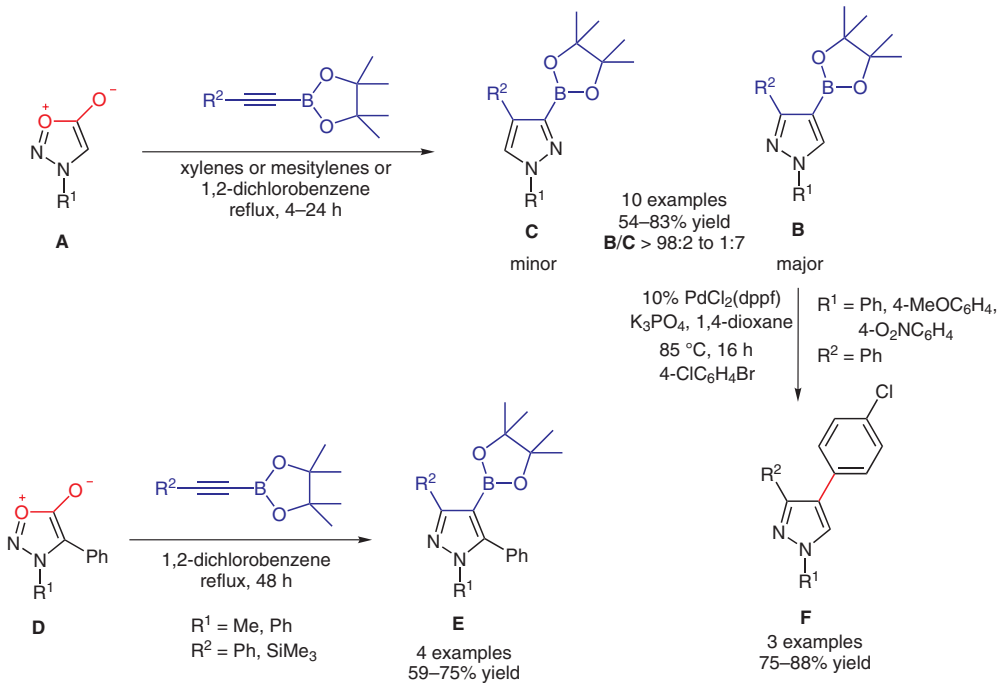
[2+3]-Cycloaddition Route to Pyrazole Boronic Esters from Sydnones and Alkynylboronates



Significance: Reported is a regiospecific synthesis of pyrazole boronic esters from alkynylboronates and N-alkyl or -aryl sydnones by cycloaddition–retro-cycloaddition reaction. The regiochemistry of the decarboxylative [2+3] cycloaddition is governed by the R^2 group of the alkynylboronate; thus pyrazole **B** predominates when R^2 = aryl, alkyl, TMS while **C** is the major product for terminal alkyne. As expected, electron-rich sydnones **A** were found to be slow-reacting (22–24 h) while more electron-deficient sydnones **A** showed significantly faster reactions (2–4 h). The cycloaddition is highly effective for sydnones **D** affording fully substituted pyrazoles **E** with complete regioselectivity. To complete the presumed reason for this study, pyrazole **B** was subjected to Suzuki cross-coupling conditions to form **F** in good yields.

Comment: Pyrazoles represent a very important class of heterocycles which are found in pharmaceutical and agrochemical substances (C. Lamberth *Heterocycles* **2007**, *71*, 1467). Although the present report appears to be the first example of alkynylboronate [2+3] cycloaddition with sydnones for the direct preparation of functionalized pyrazole boronic esters, a similar report of cycloaddition of sydnone with alkynylstannanes and alkynylsilanes has recently appeared (A. M. González-Nogal et al. *Tetrahedron* **2007**, *63*, 224). As reported herein, an alternate route rather than a metallation–boronation sequence for the synthesis of frequently unstable heterocyclic boronic acids and their derivatives is welcome.

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Category

Synthesis of Heterocycles

Key words

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N-aryl sydnones

pyrazole boronic esters

alkynylboronates