

ALTERNATING RADICAL STABILITIES. A CONVERGENT ROUTE TO TERMINAL AND INTERNAL BORONATES

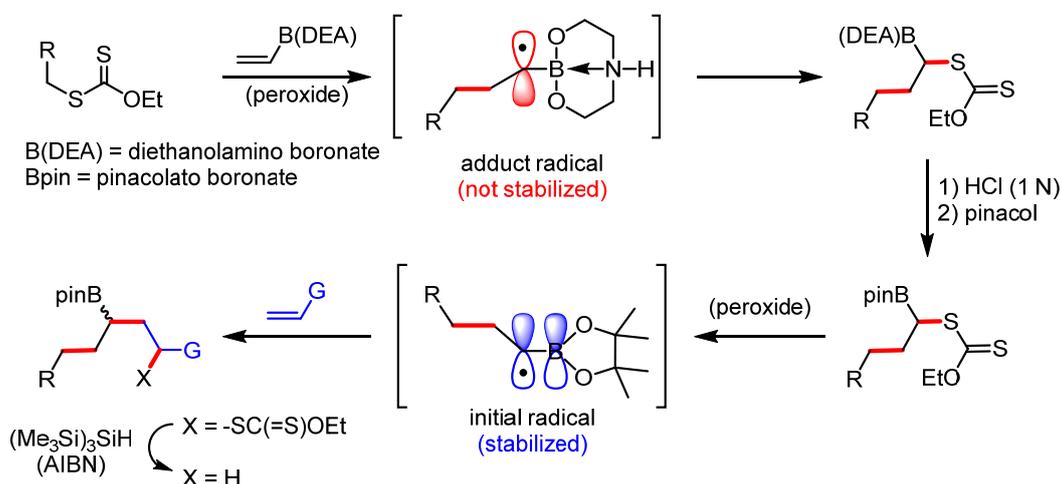
Qi Huang, Jean Michallan, Samir Z. Zard*

Laboratoire de Synthèse Organique, CNRS UMR 7652 Ecole Polytechnique,
91128 Palaiseau, Cedex, France
jean.michalland@polytechnique.edu

Boronic acids and esters have long proven their importance; in the field of catalysis, as bioactive substances or as synthetic intermediates, all thanks to the reactivity of the boron center.¹ So far, accessing such compounds has mostly relied on traditional ionic and organometallic reactions, however, radical processes have recently found interest to tackle this synthetic challenge.²

The xanthate addition-transfer process has already shown great efficiency in the construction of highly functionalized boronates.³ Its broad tolerance for polar group makes it a powerful method for the construction of previously hardly accessible organoboron compounds. However, the lack of an efficient method to obtain diverse α -boronyl xanthates has limited the study of such promising substrates.

We developed a method to tune the stability of the carbon radical adjacent to the boron to perform two successive xanthate addition-transfer reaction and obtain highly decorated boronates.³ The diethanolamino boronate, being sp^3 hybridized, does not stabilize the radical, however the pinacolato boronate stabilize the radical in alpha position thanks to its empty p-orbital. By alternating the substituent on the boron, it is possible to control the behavior of the α -boronyl xanthates and obtain a large variety of internal and terminal boronates.



[1] (a) Smoum, R.; Rubinstein, A.; Dembitsky, V. M.; Srebnik, M. *Chem. Rev.* 2012, 112, 4156. (b) Sandford, C.; Aggarwal, V. K. *Chem. Commun.* 2017, 53, 5481.

[2] (a) Matteson, S. *J. Am. Chem. Soc.*, 1959, 81, 5004. (b) Lo, J. C.; Gui, J.; Yabe, Y.; Pan, C. -M.; Baran, P. S. *Nature* 2014, 516, 343

[3] (a) Lopez-Ruiz, H.; Zard, S. Z. *Chem. Commun.* 2001, 2618. (b) Quiclet-Sire, B.; Zard, S. Z. *J. Am. Chem. Soc.* 2015, 137, 6762. (c) Huang, Q.; Zard, S. Z. *Org. Lett.* 2018, 20, 5304.

[4] Huang, Q.; Michallan, J.; Zard, S. Z. *manuscript submitted for publication*