Organoboron Compounds: Prevalent and Novel Applications

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1/16

Contents

- Introduction
- 2 Boron-Substituted 1,3-Dienes
- 3 Organoboron Compounds for SET
- Metal-Free Borylation
- 6 Annex

Characteristics of Boron¹

Table: Atomic Radii

	В	C
$r_{vdw}(\text{Å})$		1.70
$r_{cov}(\text{Å})$	0.83	0.68

Table: Bond Dissociation Energy

Bonds	D_{298K}^{o} $(kJ \cdot mol^{-1})$
B-B	290
B-H	345.2 ± 2.5
C - C	618 ± 15.4
C-H	$\textbf{318.4} \pm \textbf{1.2}$

¹David R. Lide. *CRC Handbook of Chemistry and Physics*. 90th Edition (CD-ROM Version 2010). Boca Raton, FL.: CRC Press/Taylor and Francis.

Asymmetric Reduction of $C = C^2$ and $C = O^3$ Bonds

²Herbert C. Brown, Manoj C. Desai, and Prabhakar K. Jadhav. "Hydroboration. 61. Diisopinocampheylborane of high optical purity. Improved preparation and asymmetric hydroboration of representative cis-disubstituted alkenes". In: *The Journal of Organic Chemistry* 47.26 (1982). DOI: 10.1021/jo00147a004.

³Herbert C. Brown, J. Chandrasekharan, and P. V. Ramachandran. "Chiral synthesis via organoboranes. 14. Selective reductions. 41. Diisopinocampheylchloroborane, an exceptionally efficient chiral reducing agent". In: Journal of the American Chemical Society 110.5 (1988). DOI: 10.1021/ja00213a030.

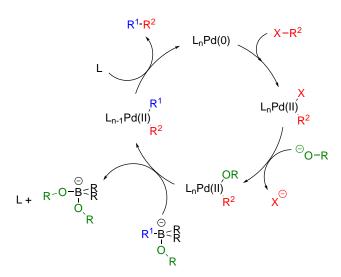
Diastereoselective Allylboration⁴

$$\left(\begin{array}{c} \\ \\ \\ \\ \\ \end{array}\right)_{2}^{B} \qquad + \qquad \left(\begin{array}{c} \\ \\ \\ \\ \\ \end{array}\right)_{O}$$

Figure: Diastereoselective Allylboration

⁴Herbert C. Brown, Krishna S. Bhat, and Ramnarayan S. Randad. "β-Allyldiisopinocampheylborane: a remarkable reagent for the diastereoselective allylboration of α-substituted chiral aldehydes". In: The Journal of Organic Chemistry 52.2 (1987), pp. 319–320. ISSN: 0022-3263. DOI: 10.1021/jo00378a042. URL: https://doi.org/10.4021/jj000378a042. **\frac{1}{2} \rightarrow \frac{1}{2} \rightarr

Suzuki-Miyaura Cross-Coupling





6/16

Tandem Diels-Alder Cycloaddition

Figure: A Module Figure

The diastereoselectivity of this two-step process is very high, that is why this process is very important for generating multiple stereocentres from rather simple starting materials.⁵

⁵ Jadwiga Pyziak, Jędrzej Walkowiak, and Bogdan Marciniec. "Recent Advances in Boron-Substituted 1,3-Dienes Chemistry: Synthesis and Application". In: 23.15 (2017). DOI: 10.1002/chem.201602124.

A Synthetic Example⁶

⁶ Alexandre Cannillo et al. "Fast Synthesis of Complex Enantiopure Heterocyclic Scaffolds by a Tandem Sequence of Simple Transformations on -Hydroxyaldehydes". In: Chemistry – A European Journal 19.28 (2013). □101.1002 (2013).

Latest application of B₂pin₂⁷

⁷Li Zhang and Lei Jiao. "Super electron donors derived from diboron". In: Chemical Science 9.10 (2018). DOI: 10.1039/C8SC00008E.

4 □ ▶ 4 □ ■ 4 □ № 4 □

Synthetic Applications of the New Method

When applied with B_2pin_2 , p-PhPy, MeOK, the following reactions can take place⁸:

⁸Li Zhang and Lei Jiao. "Pyridine-Catalyzed Radical Borylation of Aryl Halides". In: Journal of the American Chemical Society 139.2 (2017). DOI: 10.1021/jacs.6b11813.

Mechanisms of this Method

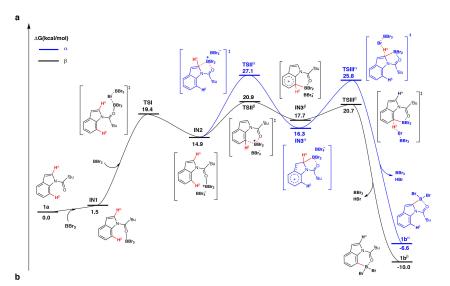
Metal-Free Directed C—H Borylation⁹

yield: 78%

yield: 99%

⁹ Jiahang Lv et al. "Metal-free directed C-H bond activation and borylation". In: Nature (2019). DOI: 10.1038/s41586-019-1640-2.

Mechanism of this Reaction



13/16

Acknowledgments

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Authors of the brilliant works mentioned above

Annex

This slide and articles cited in the slide can be found here:

https://github.com/Alexander-Qi/organoboron/releases/tag/1.0

Or Scan this QRcode:



Boryl-pyridine species and their interconversion

