



Perfunctionalised Methyl Boronates

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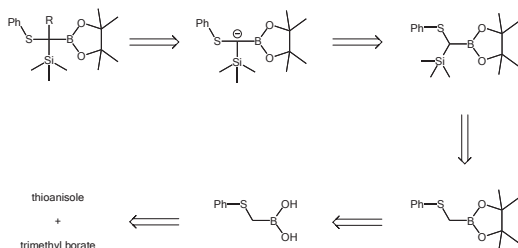
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Introduction

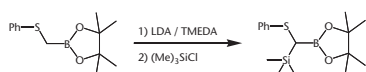
Boronates are commonly known as versatile synthetic intermediates in organic chemistry. Especially phenylthio-substituents in α -position to the boron are of major interest due to the feasibility to be converted into an iodo-functionality [1] successively opening a wide range of substitution or Matteson homologisation reactions.

Therefore, we have synthesised different highly heteroatom-functionalised carbon centres bearing a boronate substituent. It has been shown that B,S,Si -substituted carbon centres [2,3] can be easily deprotonated opening a convenient pathway to tetra-substituted carbons and highly functionalized alkenes.

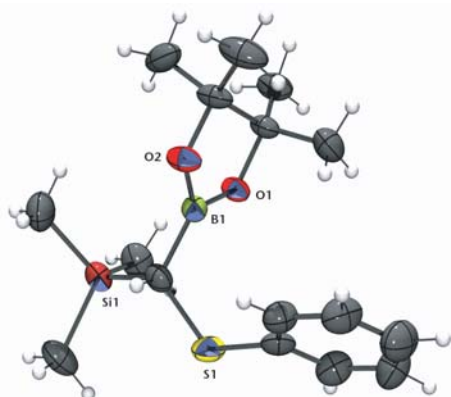
Synthetic Strategy to Perfunctionalised Methyl Boronates



Synthesis of Si,S -substituted Methyl Boronate



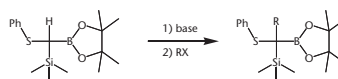
The desired tertiary methyl boronate can be synthesized in high yield from an easily available precursor [3].



Ortep Drawing of 4,4,5,5-Tetramethyl-2-((trimethylsilyl)(phenylthio)methyl)-1,3,2-dioxaborolane

Synthesis of Quarternary Substituted Methyl Boronates

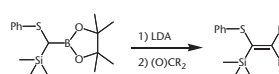
Substituted carbon centres bearing different functional groups are commonly known as interesting targets in organic chemistry. Therefore, regarding the different reaction properties of different functional groups, perfunctionalized methyl boronates can be regarded as an ideal starting point for many consecutive reactions.



Base	Reagent	Yield
<i>n</i> -BuLi	D ₂ O or (Me) ₃ SiCl	0 %
MeLi	D ₂ O or (Me) ₃ SiCl	0 %
NaH	D ₂ O or (Me) ₃ SiCl	0 %
LDA	D ₂ O	99 %
LDA	(Me) ₃ SiCl	89 %
LDA	(Me) ₃ SnCl	85 % (crude), 43 % (pure)

Peterson Olefination vs. Boron-Wittig-Reaction

Obviously, such a deprotonated Si,B -bearing carbon is predestinated to react with ketones in two different ways, namely the Boron-Wittig-reaction and the Peterson olefination. Therefore we have examined these competitive reactions showing that the Boron-Wittig-reaction is preferred.



R	Yield
methyl	92 %
phenyl	90 %

Summary

We have shown an efficient way to synthesize perfunctionalized methyl boronates. Furthermore we are now able to predict the preferred reaction pathway regarding B,S,Si -substituted carbon atoms showing that the boron-Wittig-reaction is favoured, opening a convenient route to tetra substituted alkenes.

Literature

- [1] S. Jagannathan, T. P. Forsyth, C. A. Kettner, *J. Org. Chem.* **2001**, *66*, 6375-6380
- [2] Masaki Shimizu et al., *J. Organomet. Chem.* **2003**, *686*, 286-293
- [3] D. S. Matteson, K. H. Arne, *Organometallics* **1982**, *1*, 280-288