

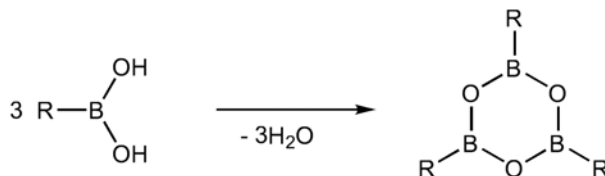
Boronic acids and their derivatives are among the most useful classes of organoboron molecules. Unlike many organometallic derivatives and most organoboranes, boronic acids are usually stable to air and moisture, and are of relatively low toxicity and environmental impact. The reactions of boronic acids can be divided into two categories according to whether the boron-oxygen or the carbon-boron bonds are involved.

Reactions involving the B-O bonds

Boroxine formation

Most boronic acids readily undergo dehydration to form cyclic trimeric anhydrides (boroxines) (Scheme 1). This tends to occur spontaneously at room temperature, so that it is difficult to obtain the acid free from the anhydride. Since in almost all cases, both will undergo the required reaction, they can usually be regarded as equivalent.

Scheme 1



Boronate formation

The ease with which boronic acids react with diols, with loss of water, to give cyclic boronic esters (boronates) has led to their application in a number of areas, especially in the carbohydrate field.

Protection of diols

One of the main applications of boronic acids has been as reagents for protection and derivatization of 1,2- and 1,3-diols as boronates (1,3,2-dioxaborolanes and 1,3,2-dioxaborinanes), particularly in carbohydrate chemistry.¹ These have been widely used as volatile derivatives for GC and GC-MS purposes. The boronate derivatives are formed simply by stirring the boronic acid and diol together at ambient temperature, by warming, or, if necessary, with azeotropic removal of water. Usually cleavage occurs readily under hydrolytic conditions, by exchange with a glycol,² or by treatment with hydrogen peroxide.³ Hindered boronic esters, such as those of pinacol, may be relatively stable to hydrolysis, and can often be purified by chromatography. A useful application of boronate protection is in the osmium tetroxide catalysed cis-dihydroxylation of alkenes under anhydrous conditions in the presence of a boronic acid.^{3b,4} Further information on the applications of boronic acids as derivatizing and protecting agents can be found in various reviews^{5,6} and monographs.⁷⁻⁹

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Other applications in carbohydrate chemistry

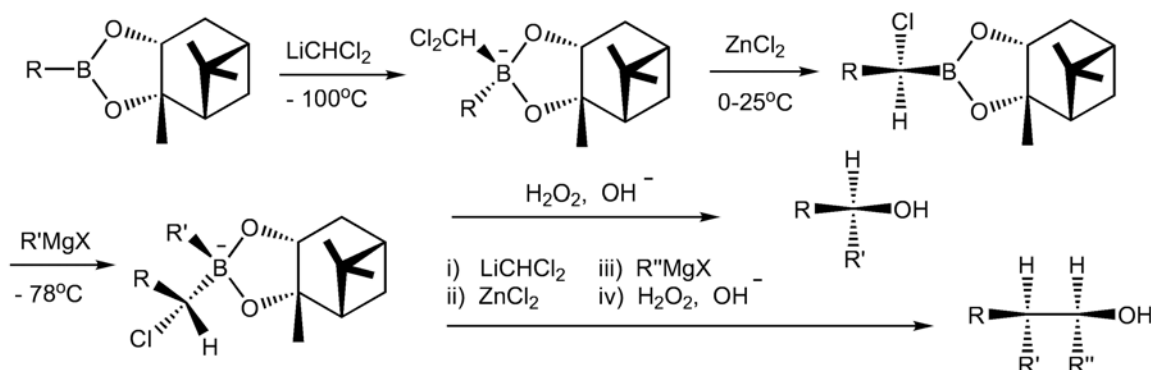
The formation of boronates with carbohydrate molecules has been utilized in numerous other applications, including the selective transport of sugars in lipophilic environments,^{10,11} and the design of artificial receptors, as discussed in several reviews.¹²⁻¹⁵

Boronic acids and esters in asymmetric synthesis

Chiral boronates

Matteson has carried out extensive work on cyclic boronates,^{16,17} formed from chiral diols such as (1S,2S,3R,5S)-2,3-pinandediol or (R,R)-(-)-2,3-butanediol, which undergo carbon insertion with LiCHCl_2 in the presence of zinc chloride in up to 99% diastereomeric excess (de). Treatment of the resulting α -chloro boronic esters with various nucleophiles leads to α -substituted boronic esters which can be deprotected with hydrogen peroxide, or the sequence can be repeated to introduce a second chiral center, as illustrated in Scheme 2.

Scheme 2



Oxazaborolidines

Reaction of various boronic acids with chiral amino alcohols gives oxazaborolidines, which were introduced by Corey as excellent catalysts for enantioselective borane reduction of ketones with very high ee.¹⁸ The reagents derived from α,α -diphenylprolinol have received the most attention, although the use of other amino alcohols has also been reported.^{19,20} For further details, reaction scheme and references, see under (S)-(-)- α,α -Diphenylprolinol, (S)-2-Methyl-CBS-oxazaborolidine monohydrate and n-Butylboronic acid in the main Catalogue. Reviews on the use of oxazaborolidines as enantioselective catalysts,^{21,22} and the asymmetric reduction of ketones^{23,24} are available.

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Diels-Alder reactions

Boronic acids form stable chiral acyloxyborane (CAB) catalysts with tartaric acid derivatives, which have been developed by Yamamoto as catalysts for asymmetric Diels-Alder²⁵ and hetero Diels-Alder²⁶ reactions, for example between aldehydes and Danishefsky's Diene [1-methoxy-3-(trimethylsiloxy)-1,3-butadiene; L06100, L14672], to give enantioselectively, dihydro-4-pyrone derivatives.²⁷

For the use of a boronic acid template in stereocontrolled Diels-Alder reactions,²⁸ see under Benzenboronic acid in the main section of the Catalogue.

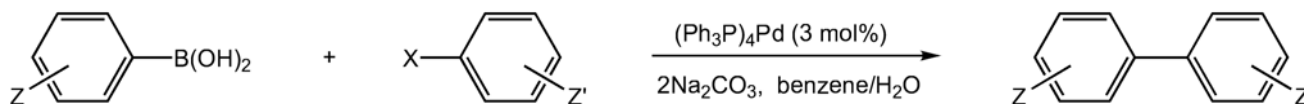
Reactions involving cleavage of the C-B bond

In these reactions, displacement of boron by an electrophilic species takes place with formation of a new carbon-carbon or carbon-heteroatom bond.

C-C bond forming reactions: Suzuki biaryl coupling

The discovery by Suzuki and Miyaura²⁹ that arylboronic acids undergo palladium-catalyzed cross-coupling with aryl halides in the presence of a base (Scheme 3) has stimulated enormous interest in the application of this (the Suzuki reaction), and variants developed subsequently, to the synthesis of unsymmetrical biaryls and related compounds.

Scheme 3



Many of the methods previously employed for such syntheses involve the direct coupling of highly-reactive organometallic reagents (Grignard, organolithium, etc.) with aryl halides in the presence of various catalysts. Such reactions are of limited utility, since the presence of many functional groups interferes. Boronic acids, on the other hand, which are air-stable materials of relatively low toxicity, will undergo the Suzuki reaction in the presence of a wide variety of functional groups. The highly versatile Stille coupling reaction,³⁰ by comparison,³¹ involves toxic organotin species. Under the standard coupling conditions, aryl bromides are most frequently used as the electrophilic species, but iodides are more reactive. The successful coupling of the more readily available, but normally unreactive aryl chlorides has been achieved under modified conditions, using either palladium³² or nickel³³ catalysts. A catalytic cycle for the Suzuki reaction^{34,35} is outlined in Scheme 4. A detailed mechanistic study has also been published.³⁶

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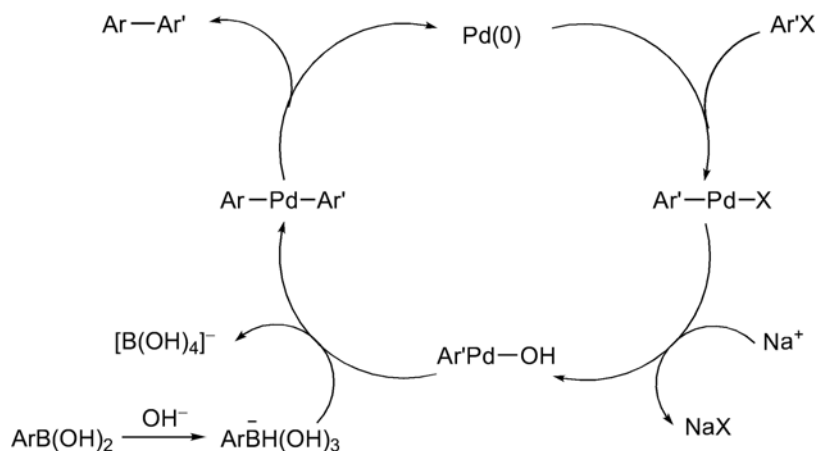
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Scheme 4



Alternative illustrative experimental procedures for the biaryl synthesis have been reported in *Organic Syntheses*.³⁷ Useful reviews of the Suzuki and related reactions have been published by Suzuki and Miyaura^{38,39} and by Martin and Yang,³⁵ and of biaryl synthesis via cross-coupling reactions by Stanforth.⁴⁰ The more recent literature has been reviewed by Kotha *et al.*⁸⁸

Related coupling reactions

A variety of heterocyclic halides have been coupled with boronic acids, including thiophenes,⁴¹ furans, thiazoles,⁴² isoxazoles,⁴³ pyridines,^{44,45} pyrimidines^{42,44} and pyrazines.^{44,45} Aryl or vinyl triflates can undergo palladium-catalyzed boronic acid coupling, which usefully extends the scope of the reaction to phenols or enols.⁴⁶⁻⁴⁸ Coupling of boronate derivatives with aryl mesylates, catalyzed by nickel complexes, has also been reported,^{49,50} as has palladium-catalyzed coupling with sulfonium salts.⁵¹ Arenediazonium tetrafluoroborates have been found to undergo coupling with arylboronic acids in dioxane or methanol, catalyzed by palladium acetate in the absence of both added base and phosphine ligand.⁵² This has been extended to the coupling of arenediazonium tetrafluoroborates with potassium aryltrifluoroborates,⁵³ which are more nucleophilic than the corresponding arylboronic acids, and also with potassium vinyl trifluoroborates,⁵⁴ which are air-stable crystalline solids, more readily prepared and isolated than the corresponding vinylboronate esters. Alkenyl and aryl trifluoroborates have also been reported by Molander to couple with aryl halides, which greatly extends their usefulness.⁸⁹

Coupling of arylboronic acids with, for example vinylic halides,^{55,56} or allenyl methyl carbonate,⁵⁷ have also been described.

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