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A Study on Scope and Developments of Organic Synthesis in Boric Acid

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Abstract – Boric acid [H3BO3] was a central element in organic synthesis in recent years. This review provides a summary of recent developments in the fields of catalyzed boric acid transformation in particular sterilization, trans esterification, addition of aza-Michael and thia-Michael, condensation, friedal reactions, halogenation, ipso substitution, decarboxylation, protection and deprotection, amidation and transamination reactions, multicomponent reactions, and more. In forming various biologically significant organic compounds recorded during the last decade, boric acid has emerged as an effective, mild, commercially available, inexpensive catalyst.

Keywords: Acid Catalysis, Boric Acid, Heterocyclic, Organic Synthesis

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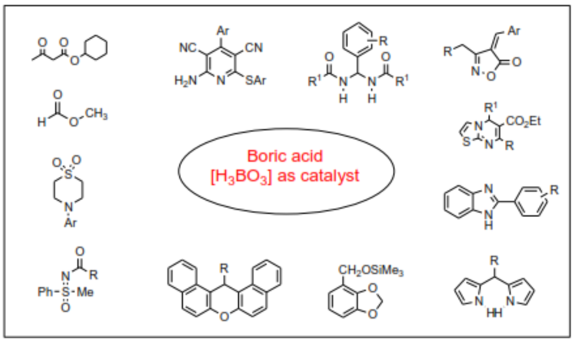
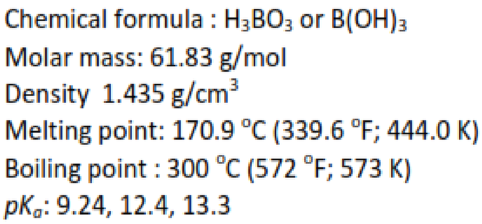
INTRODUCTION

In the last decade, boric acid chemistry has developed rapidly. This increasing interest is primarily due to its mild and highly selective properties and the ecologically mild nature and availability. In organic synthesis, boric acid is now routinely used in various selective transitions in single and complicated molecules as effective acid catalytic. The aim of this analysis is to tie together the utility of boric acid in recent synthetic applications. It's up to the end of 2017 to cover literature.



Boric acid, also referred to as boric acid or orthoboric acid, is a heavy, inorganic acid. It is a white crystalline solid with physical characteristics:


Chemical formula : H_3BO_3 or $B(OH)_3$
Molar mass: 61.83 g/mol
Density 1.435 g/cm^3
Melting point: 170.9 °C (339.6 °F; 444.0 K)
Boiling point : 300 °C (572 °F; 573 K)
pK_a: 9.24, 12.4, 13.3

Solubility: Soluble in water and in lower alcohols; moderately soluble in pyridine; very slightly soluble in acetone

Figure 1A shows that three classes of hydroxy (-OH) that have the ability to bind heavy hydrogen are connected to the central boreal atom. The solid crystalline structure consists of parallel layers of hydrogen-bonded boric acid (Figure 1B). It is used as a low mono-basic acid source. It was used in various catalytic acid reactions. The boric acid content is not dangerous and is easy to handle and safe to use. It is also used in acne, preservative, insecticide, pH tap, as a pool chemical and as precursor to many useful chemical products. It also works as an antiseptic agent.

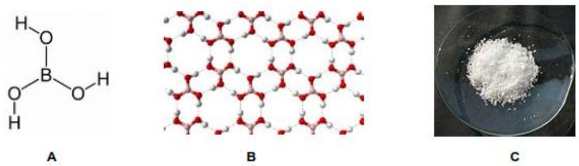
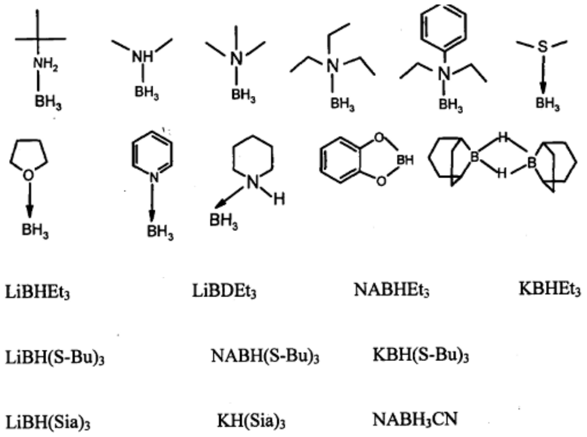
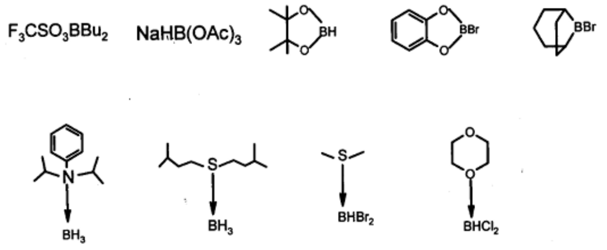


Figure 1. Structure of boric acid (A), parallel layers in solid state (B) and view of crystalline state (C)

Hundreds of further useful reagents based on boron have been found in H. H. In the 20 + years following his 1979 Nobel Prize victory, C. Brown's laboratories are maintained at Purdue. Within this short account, you cannot mention all these newer reagents. The main organo boron partners (especially in the cross-coupling-type Suzuki Miyaura reactions) are boron acids, boronate esters and organoboran for many years. Over the past decade, the use of boron reagents, in particular boric acids, has expanded considerably, with researchers finding a wide range of applications for these diverse compounds. They are used as carbohydrate sensors4 and bio conjugates in sugar-permeable membranes. The use of boron neutron capture therapy and as therapeutic agents also includes research into boron acids. In Suzuki coupling reactions the use of Boric acids in the cyclic cis- and tram separation of 1,2-diols 11 'and, on occasions, as precursor of boron enolates is used in synthetic applications.



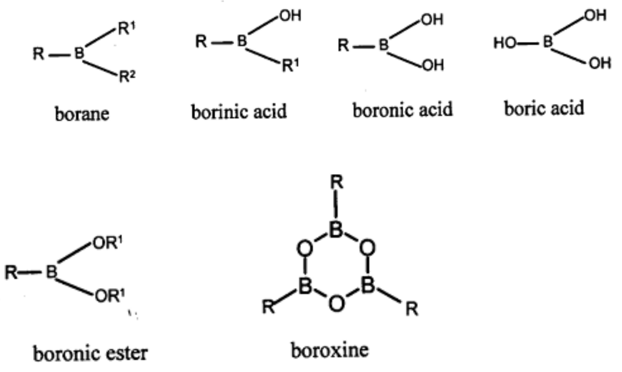
Apart from these, hundreds of additional and useful boron based reagents were discovered. The following figure gives the representative list of the latest borane reagents such as;



Here, in this account we discuss Boric acid as a major aspect from the family of boron reagents and boronate esters.

BORIC ACIDS

Structural boric acids are three valent organic compounds borons that have an alkyl substitution (i.e. a bond with a C-B) and two hydroxyl groups to complement the remaining atomic valences.



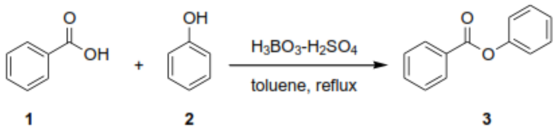
In comparison to carboxylic acids, boric acids do not exist in nature, their carbon analogs. These abiotic compounds are synthesized by primary boron sources, such as boric acid, caused by carbon dioxide acidification of borax. It is made from a simple dehydrating of boric acid with alcohols the boric esters, the key precursors for boric acid derivatives. Boric acids are a particularly attractive class of synthetic intermediates due to the unique properties of mild organic Lewis acids and their mitigated reactivation, combined with their stability and ease of use. Boric acids are often known to be "natural" compounds because they are low in toxicity and eventually dissolved in the environmentally friendly boric acid.

REACTIONS TO ESTERIFICATION

Esterification is one of the oldest, most widely used and the most effective organic synthesis chemical transformations, with wide applications for chemical, pharmaceutical, food, perfume and cosmetic industries. Such reactions refer to natural product synthesis, carboxylic acid safety or kinetic resolution, and intra-molecular lactone-preparation reactions. Carboxylic acid esterification, hydroxy acids, sugar acids and boric acid were studied.

1. Carboxylic acid esterification

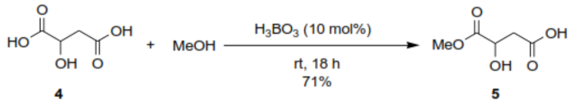
Aliphatic and aromatic carboxylic acids are directly esterified with the phenols of boric acid and sulfuric acid. None of the reactions catalyze boric acid nor sulfuric acid either. Therefore, phenyl Benzoate (3), which includes phenol, benzoic acid and catalytic amounts of boric acid and sulfuric acid, has been generated in a nearly quantitative yield by azeotropic distillation.



Scheme 1. Catalyzed boric acid carboxylic acid esterification

2. α-hydroxy acid esterification

Houston and colleagues reported the selected esterification for α-hydroxy acids with boric acid.2 When malic acid (4) (a dicarboxylic acid with an α-position α-position hydroxyl acid and β-position β-position) and methanol were allowed to react with boric acid at room temperature overnight, a high production of monoester 5 was obtained. The group -CO2H remained unchanged as for the group β-hydroxy. The α-OH group was discussed with regard to carboxylate. During the reaction, one cyclically neutral five member Ester 6 and one anionic species 7 can be formed (Figure 2).



Scheme 2. α-hydroxy acid synthesis of Boric acid Catalyzed Methyl ester

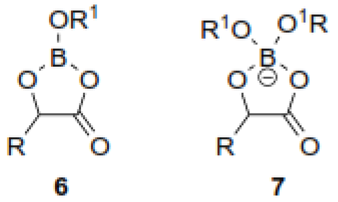
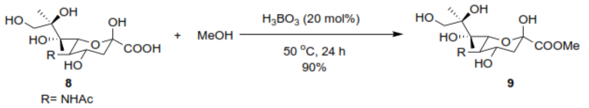


Figure 2. Possible intermediates of α-hydroxy acid esterification compounds 6 and 7

3. Sugar acid esterification

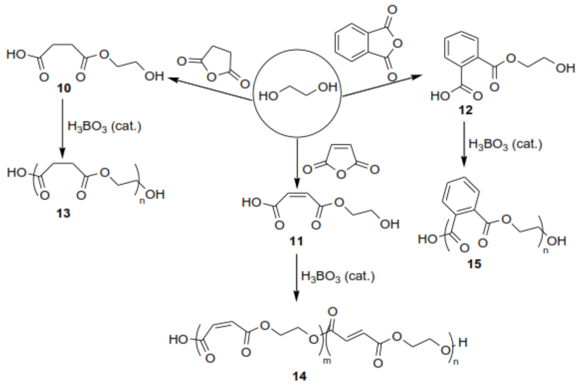
In presence of boric acid, sugar acids are esterified with methanol. Thus, in presence of the catalytic volume of boric acid in the nitrogen atmosphere at 50, Methyl ester 9 was formed in 90% yield (scheme 3) when sialic acid (8) (sugar acid)) was treated with the use of anhydrous methanol. Such reactions in certain sugar acid molecules were highly efficient but highly dependent on substrates. Glucuronic acid contains a β-hydroxycarboxylate, and the 3-deoxy-D-manno-oct-2 (KDO) bacterial monosaccharide motif has failed to esterify under methanol boric acid catalysis.



Scheme 3. Esterification of Sialic Acid and Boric Acid Catalysis (8)

4. Monohydroxyethyl ester polyesterification of dicarboxylic acids

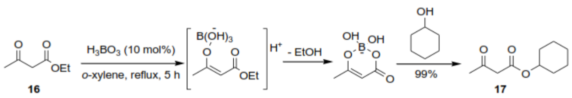
Alemdar and others 4 have concluded that the blend of boric acid-pyridine is used in the polyesterification of succinic 10, maleic 11 and phthalic acid monohydroxyethyl esters 12. Colourless polyesters 13, 14 , 15 of low molecular weight (M: 1650-1950) were demonstrated to be produced within four hours at 130o C (Scheme 4).



Scheme 4. Monohydroxyethyl ester polyesterification of 10, 11 and 12 boric acid esters

REACTIONS TO TRANSESTERIFICATION

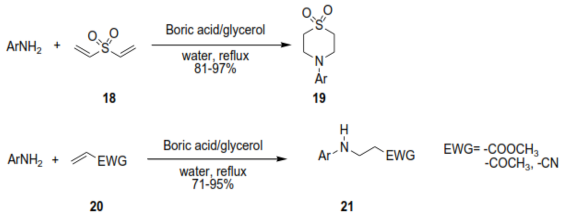
Boric acid was reported for transesterification of esters with alcohol. Boric acid is stated by Kondaiah and his collaborators as an ecologically friendly catalyst for transesterification of ethyl acetoacetate (16) with a range of alcohols including allylic alcohol, propargyl alcohols and strong to excellent yields from primary and secondary sterically impaired alcohols. The transesterified β-ketoester 17, used in refluxing xylene, can be prepared from ethyl acetoacetate (16) and cyclohexanol. (Regulation 5).



Scheme 5. Catalyzed transesterification reactions postulated mechanism of boric acid

Aza-Michael Addition Reactions

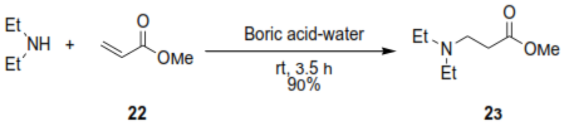
Aza-Michael has been performed in the presence of boric acid / glycerol in reflux water to obtain the corresponding additional products at strong to excellent performance without polymerisation in divinyl sulfone (18) and electron-deficient alkenes (20). Aza-Michael The method can also be used for the development of thiomorpholine substitute 1,1-dioxides 19, β-amino esters / ketones / nitriles 21, respectively, from compounds 18 to 20 (Scheme 6).



Scheme 6. Aza-Michael additional reactions catalyzed by boric acid

Chaudhuri et al. have used boric acid (10 mol percent) in the water at room temperature as

Michael-based donors (22) to provide moderate to high yields for the corresponding aza-Michael-based additional product 23 (schemes 7). Chaudhuri et al.



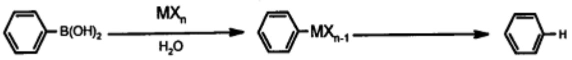
Scheme 7. Aza-michael catalyzed aza-boric acid added amine to α β -methyl ester

BORIC ACID DERIVATIVES REACTIONS

1) Catalyzed protodeboronation metallisation and alloy

Michaelis and Becker (1982) The phenyl mercuric chloride preparedness from the phenyl boric acid and aqueous mercury chloride reaction has been identified. Benzyl Boric acid is also converted into benzyl mercuric chloride, and under the conditions of its preparation both compounds were observed to be resistant to hydrolysis. Mechanical experiments later demonstrate that the hydroxyboronate ion is active. Catechol and pinacol alkenyl Boric esters can also easily be converted to the correct organic mercurial derivatives with structure retention. Several metal ions [except Hg (II)] that lead to protodeboronation in water, possibly through the intermediate intermediary phase of a species of arylmetals. In the same conditions, alkyl boric acids were not reactive.

Cu(II)>Pb(II)>Ag(I)> Cd(II)>Zn(II)>CO(II)>Mg(II)>Ni(II).

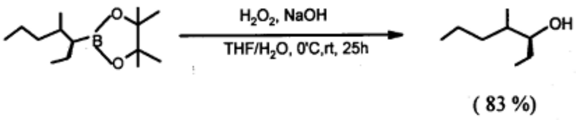


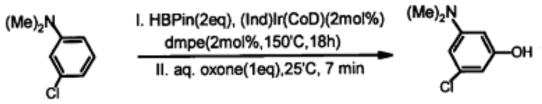
$MX_{n-1} = HgCl$

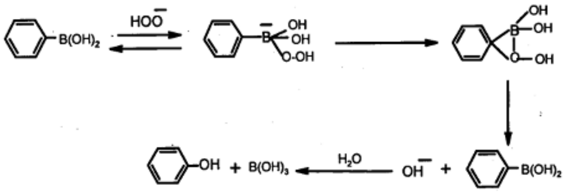
BORON OXIDATIVE SUBSTITUTION

A) Oxygenation

The first reported phenols were the treatment of aryl boric acids and esther with alkaline hydrogen peroxide more than 75 years ago. Alkanols16 and aldehydes / ketones are respectively produced by the oxidation of alkyl and alkenyl-boric acid derivatives. The reaction takes place by retaining the configuration with a-chiral alkylboronates. Nonetheless, boric and ester oxidation is synthetically useful; paradoxically the oxidation of aryl Boric acids is not a common and economic approach when preparing chiral aliphatic alcohols through asymmetric hydroborative reactions. It was recently reported to provide access to meta stabilised phenols, which would be difficult to obtain by other means, to a single pit activating / borylating / oxidizing C-H series. Kuivila investigated the mechanism of the aqueous fundamental oxidation of phenyl boric acid.

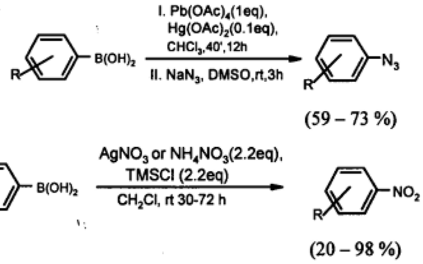


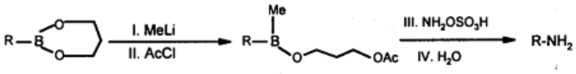




B) Amination

Indirectly aryl azides can be produced by the in situ intermediates of aryl boric acids. A mild technique has been recently developed and a method has been proposed for ipso-nitration of arylBoric acids. Boric acids and their esters do not affect the raising methods and reagents for electrophylic amination. Such processes require more electrophilic boron substrate intermediate treatment, such as boric acids or dicloroborans.



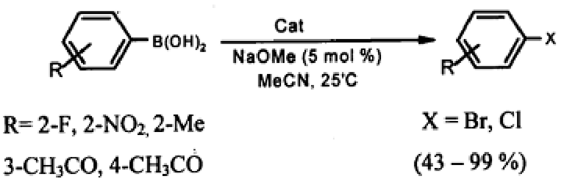


HALOGENATION

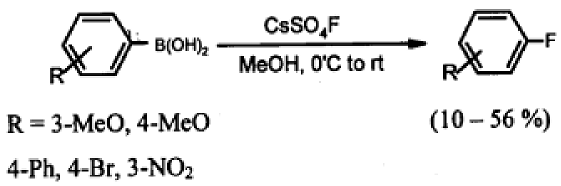
A) Boric acids and esters in Aryl

As stated earlier, the ipso substituted phenyl halides of benzene Boric acids are given by cuprous chloride and bromide. Likewise, the symptoms of aqueous chlorine, bromine and iodine containing potassium iodide are a halodeboronate of boric acids. Under the same conditions, alkyl boric acids do not react.

Aryl boric acids are converted into the respective halides with a strong to excellent yield by N-bromo and N-iodosuccinimides. The majority of aryl boric acids lead to the refluxation of acetonitrile where 2-methylphenyl boric acid is iodinated at room temperature as the most active acids. L,3-dibromo-5,5-dimethyl hydantoïne [DBDMH] has recently been found to be an effective form of bromodeboronization in the use of aryl boric acids in catalysis by sodium methoxide when solvent acetonitrile is used.

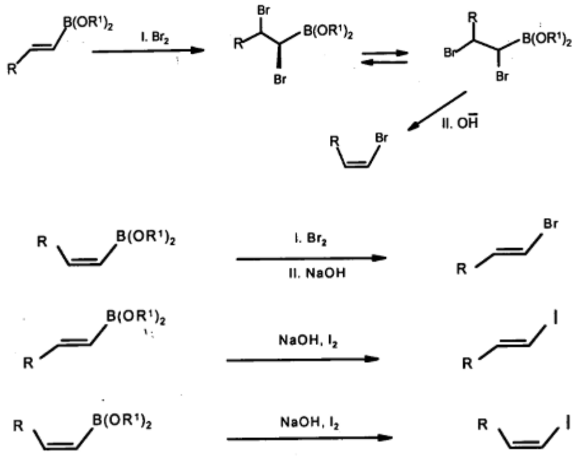


Aryl fluorides can be obtained in modest yield by treatment of aryl Boric acids with Cesium Fluoroxysulfate($CsSC_4F$) in methanol.



B) Boric acids and esters of alkenyl

The bromine bromide in the ethereal anhydroous solution, alkenyl boric acids, or alcohol in a single bath, provide olefine structure reversal to the corresponding alkenyl bromides. The inversion process is based on the formation of a nearby dibromide, which is accompanied by trans bromodeboronation, supported with the addition of the base and complementary to iodinolysis, which gives alkenyl iodides with olefin structure retention.



CONCLUSION

This analysis provides an overview of the active role of boric acid as a catalyst for synthetic applications. This growing interest in boric acid is mainly due to its very useful acidic properties and its benign environmental character and economic efficiency. In several fields of catalytic boric acid chemistry, activity has increased significantly. This includes the application of boric acid to different organic transformations such as C-C, C-N, and C-O and C-S connections in different compounds of synthetic importance. The current analysis is considered to have an effect on the continued production of catalyzed organic boric acid transformations as it is one of the driving forces for today's organic methodologists worldwide.

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