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Boron Sulfonic Acid (2008-2012)

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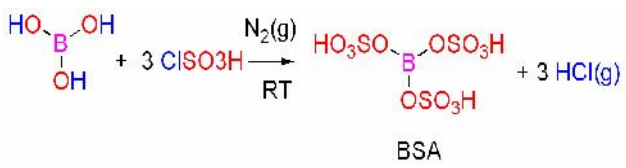
Abstract: Pproduction and application of boron sulfonic acid (BSA) and its behavior in organic synthesis as a trifunctional ionic liquid in this review article has been discussed.
Keywords: Boron sulfonic acid (BSA), Silica boron sulfonic acid (SBSA), Organic synthesis, Catalyst.

1.Introduction

Recently more attention has been paid to the application of inorganic acidic salts in organic synthesis [1,2]. Solid acids have many advantages such as simplicity in handling, decreased reactor and plant corrosion problems, and more environmentally safe disposal in different chemical processes. Also, wastes and by-products can be minimized or avoided by using solid acids in developing cleaner synthesis routes.

Boron sulfonic acid (BSA) as a novel solid acid catalyst was introduced by Kiasat *et al.* (Scheme 1) and used it for the regioselective conversion of epoxides to thiocyanohydrins under solvent-free reaction conditions [3]. BSA should be supported by silica gel so it's another name is silica boron sulfonic acid (SBSA).[4,5] Boron sulfonic acid as a trifunctional inorganocatalyst is strong acid and soluble in water and polar solvent.



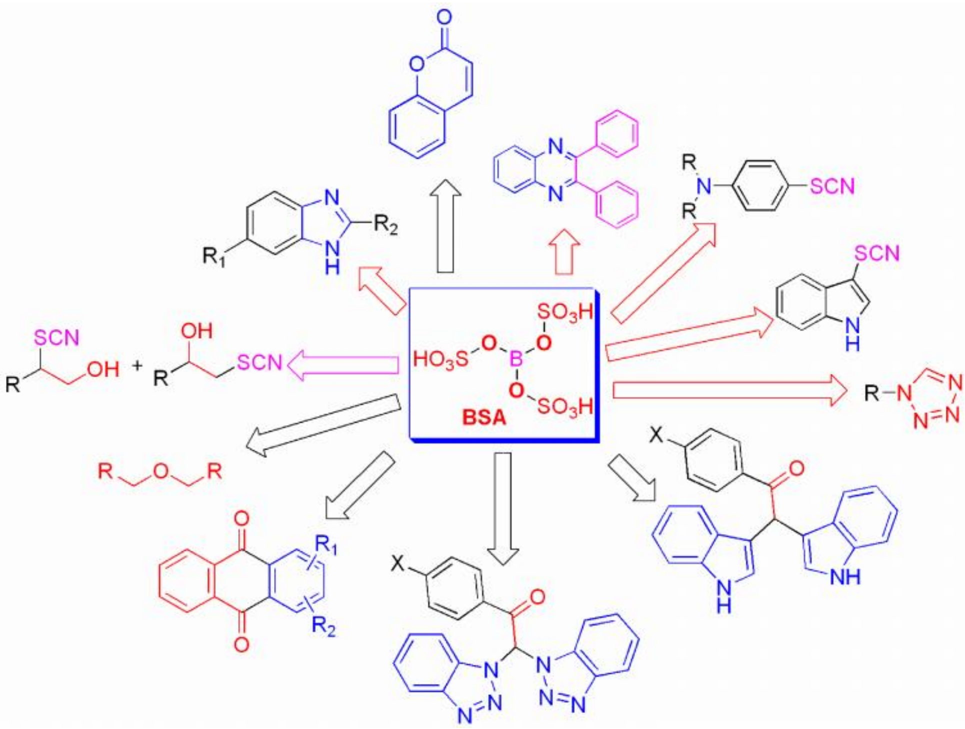
Scheme 1.

Abbreviations

BSA	=	Boron sulfonic acid
SBSA	=	Silica Boron sulfonic acid
TMB	=	Trimethyl borate
STMB	=	Silica Trimethyl borate
TIPB	=	Triisopropyl borate
STIPB	=	Silica Triisopropyl borate
$BTSA.SiO_2$	=	Silica supported boric trisulfuric anhydride

2. Preparation

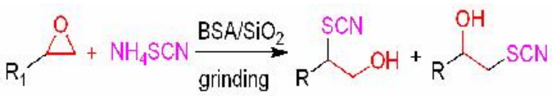
Boron sulfonic acid was easily prepared by addition of chlorosulfonic acid to boric acid under N_2 atmosphere at room temperature [3-10]. This reaction was easy and clean, because HCl gas was evolved from the reaction vessel immediately (Scheme 1). In fisrt, the catalytic ability of $B(HSO_4)_3$ was examined for conversion of epoxides to corresponding thiocyanohydrins.



Scheme 2.

3.1. Regioselective conversion of epoxides to thiocyanohydrins

Kiasat *et al.* described successful results that led to an extremely convenient method for the transformation of epoxides into the corresponding β-hydroxy thiocyanates using NH_4SCN and in the presence of $B(HSO_4)_3$ as solid acid catalyst in solvent-free process in high isolated yields. According to obtained results, this catalyst acted very efficiently and only 0.3 mmol of the catalyst is enough to convert different epoxides (1 mmol) carrying electron donating or withdrawing groups to their corresponding β-hydroxy thiocyanates in high isolated yields (Scheme 3) [3].



Scheme 3.

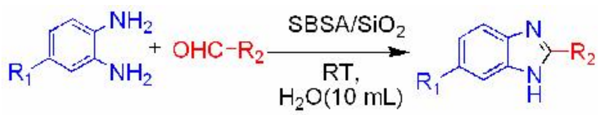
3.2. Quinoxaline synthesis

BSA is a useful catalyst for green quinoxalines synthesis [4]. 1,2-phenylendiamine and 1,2-dicabonyl compounds were reacted in presence amount of BSA(3 mol%) in water at room temperature in high yield(80-98%)(Scheme 4) [6,7].

Scheme 4.

3.3. 2-Substituted benzimidazole synthesis

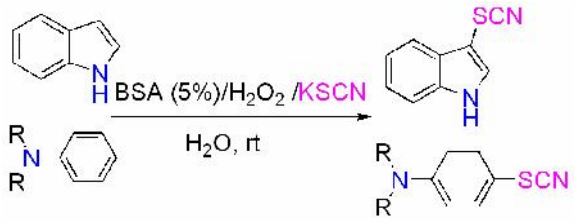
1,2-Phenylendiamine and aldehydes were reacted in presence amount of BSA (5 mol%) in water at room temperature in good to excellent yield [4,5]. For more purification of products, we used preparative plate (Scheme 5).



Scheme 5.

3.4. Thiocyanation of aromatic and heteroaromatic compounds

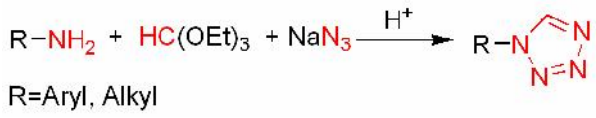
A green and simple procedure for the thiocyanation of aromatic and heteroaromatic compounds in the presence of a catalytic amount of BSA in water is described. The reactions proceed in high yields, short reaction times and mild conditions (Scheme 6) [9-12].



Scheme 6.

3.5. 1-Aryltetrazole synthesis

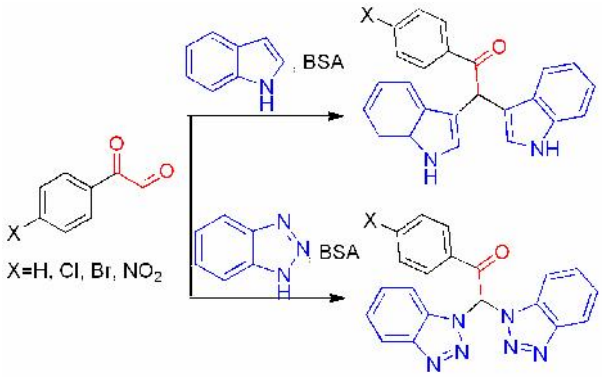
We prepared 1-aryltetrazoles by reaction of arylamines, triethyl orthoformate, and sodium azide by using boron sulfonic acid as a new, cheap and efficient catalyst in ethylenglicol at high temperature (Scheme 7) [13].



Scheme 7.

3.6. Syntheses of bis(1H-indol-3-yl)ethanones and bis(benzotriazolyl)ethanones

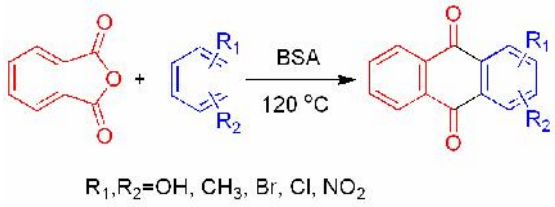
Mosslemin *et al.* was discribed an efficient syntheses of bis (1H-indol-3-yl)ethanones and bis (benzotriazolyl)ethanones via reaction of phenylglyoxals with indole or 1H-benzotriazole in the presence $B(HSO_4)_3$ in solvent-free thermal and in aqueous media conditions. The syntheses have several advantages such as: generality, short reaction time, simple experiment and work-up procedures, excellent isolated yields (Scheme 8) [14].



Scheme 8.

3.7. Synthesis of anthraquinone derivatives

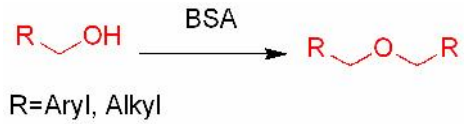
Madje *et al.* catalyzed an efficient synthesis of anthraquinone derivatives from phthalic anhydride and substituted benzenes by using boron sulfonic acid $B(HSO_4)_3$ under solvent free condition in good to excellent yields (70-96%) (Scheme 9) [15]. This method provides several advantages such as environmental friendliness, a simple procedure, mild conditions, and much faster (60-120 min) reactions.



Scheme 9.

3.8. Preparation of ethers

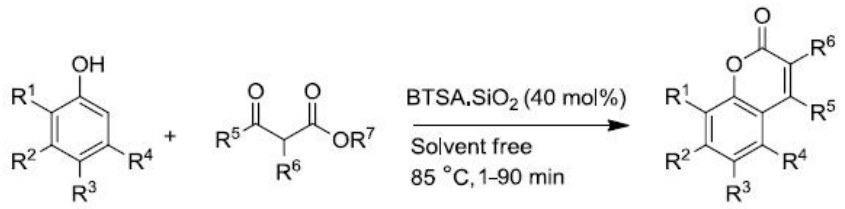
Boron sulfonic acid was supported on silica gel by simple grinding and used as efficient solid acid catalyst in the preparation of ethers from the aliphatic and aromatic alcohols. The ethers were prepared in high isolated yields and in lesser times (Scheme 10) [16].



Scheme 10.

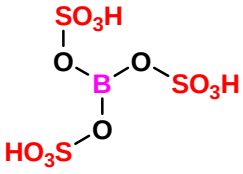
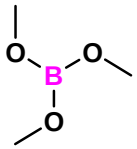
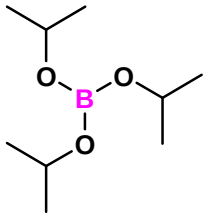
3.9. Synthesis of coumarins via Pechmann condensation

Silica supported boric trisulfuric anhydride (BTSA.SiO2) (another name of BSA) is a novel, suitable and versatile catalyst for efficient and clean synthesis of coumarins via Pechmann cyclocondensation under mild and solvent-free conditions. Different kinds of phenols and β-ketoesters were subjected to the cyclization reaction. Particularly, this catalyst makes the condensation of less activated phenols feasible. Besides the described benefits, the reported catalyst was applied successfully for the synthesis of novel coumarins from 3-acetyldihydrofuran-2(3H)-one as well as estradiol (sex hormone) (Scheme 10) [17].



Scheme 10.

Table 1. Comparison boron central catalysts

Structure of catalysts			
Name of catalysts	Boron sulfonic acid **BSA**/SiO_2	Trimethyl borate (**TMB**)/SiO_2	Triisopropyl borate (**TIPB**)/SiO_2
Time(h:min)	00:05	20:00	28:00
Yield%	98	94	91

4. Study of the BrØnsted acidic power Contrast with Levis acidic power

BSA has two character of acidity power. The end of $–SO_3H$ has BrØnsted acidic power and boron atom with vacuum orbital has Levis acidic power but BrØnsted acidic power of BSA is more prevailing. We used silica supported BSA, TMB and TIPB for synthesis of 2,3-diphenylquinoxaline and results of this comparison is summarized in Table 1.

5. Conclusion

Boron sulfonic acid have been the most commonly used in liquid-, solid-phase (solvent-free thermal)[12] as a more efficient, cheap and green catalyst and trifunctional inorgananic strong acid. For easily handling of BSA, silica gel supported it.

Acknowledgment

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