Research Progress on Nitrification of Boric Acid and Borate

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Abstract: Boric acid compounds and their salts are widely used in organic synthesis due to their structural diversity, insensitivity to water and air, good tolerance of functional groups and green environmental protection. The recent progress in the synthesis of nitro compounds using boric acid and borate as raw materials was reviewed.

Keywords: Boric acid, nitrification, nitro compounds

1.Introduction

Nitrocompounds are a class of very important compounds, widely used in many fields, as well as important intermediates in the pharmaceutical industry. The nitrocompounds can be converted into amines, isocyanates or carbamate [1], ketones or aldehydes (Nef reaction)[2], and heterocyclic indole [3].Therefore, the synthesis of nitro compounds has attracted much attention. Traditional nitrification synthesis methods mainly include nitric acid nitrification [4], nitrate-sulfur mixed acid nitrification [5], nitric acid-acetic anhydride [5], N_2O_5 [6], etc. The traditional method of nitrification synthesis has obvious shortcomings, such as harsh reaction conditions, high requirements for equipment, and more waste. Therefore, the development of green chemical nitrification method is particularly important.

Boric acid compounds and their salts are widely used in organic synthesis, such as Suzuki [7] reaction, Chan-evans-Lam [8] reaction, asymmetric addition of aldehydes and ketones [9] reaction, etc., due to their structural diversity, insensitivity to water and air, good tolerance of functional groups, and low toxicity.The progress of nitrification with boric acid and borate as raw materials in recent years is reviewed.

2. Boric acid as raw material in the application of nitrification reaction

In recent years, the nitrification reaction with boric acid as raw material has developed rapidly, and many synthetic methods have emerged. In 2000, Prakash, Petasis and Olah et al. [10] reported for the first time that the nitrification of aromatic boric acid was achieved using ammonium nitrate and trifluoroacetic anhydride as nitrification reagents and acetonitrile as solvent (Figure 1) with a yield of 23-78%. It was found that the nitrification products were generated in the reaction process, and the amount of nitrification products increased when the amount of nitrification agent was increased.

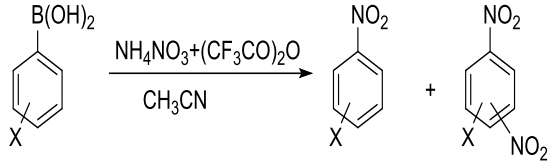

Figure 1. Nitrification of aromatic boric acid by using ammonium nitrate and trifluoroacetic anhydride

In 2004, Prakash and Olah et al. [11] reported that the nitrification of aromatic boric acid was achieved using silver nitrate (ammonium) and trimethylchlorosilane as nitrification reagents and methylene chloride as solvent (Figure 2), with a yield of 20%-98%. This method is simple, has good selectivity, mild reaction conditions, and can get medium to high yield at room temperature. However, the yield of m-nitro and trifluoromethyl substituted phenylboric acid is low.

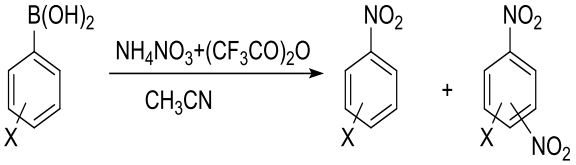

Figure 2. Nitrification of aromatic boric acid by using silver nitrate (ammonium) and trimethylchlorosilane

In 2011, Fu et al. [12] reported that using sodium nitrite as nitrification reagent, cuprous oxide and ammonia water as catalytic system, the nitrification reaction of aromatic boric acid in water phase was realized (Figure 3) with the yield of 44-70%.It is worth noting that the copper catalytic system can be recycled multiple times.

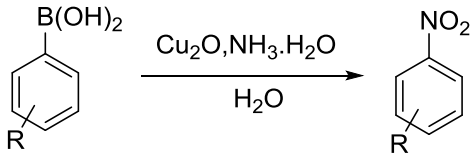

Figure 3. Nitrification of aromatic boric acid by using sodium nitrite as nitrification reagent

In 2011, Wu and Beller et al. [13] reported that the nitrification of aryl boric acid was achieved using terbutyl nitrite as nitrification reagent and 1, 4-dioxane as solvent (Figure 4), with a yield of 45%-87%.The

advantage of this reaction is that no catalyst is used.

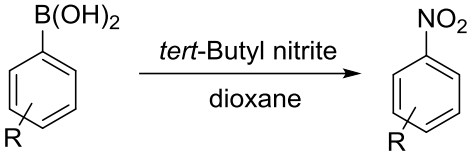

Figure 4. Nitrification of aromatic boric acid by using terbutyl nitrite as nitrification reagent

In 2012, Yan et al. [14] reported that the nitrification reaction of aromatic boric acid was realized using sodium nitrite or ammonium tetrabutylnitrite as nitrification reagent, cuprous oxide as catalyst and acetonitrile as solvent (Figure 5), and the yield was TRACe-88%. Copper catalyst was screened by this method and cuprous oxide was the best catalyst.In the same year, the same research group [15] developed a catalyst free, using terbutyl nitrite as the nitrification reagent, and realized the controllable nitrification and nitrification reaction of aromatic boric acid (Figure 6).

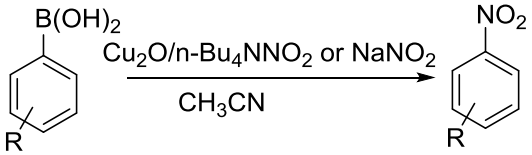

Figure 5. Nitrification of aromatic boric acid by using sodium nitrite or ammonium tetrabutylnitrite as nitrification reagent, cuprous oxide as catalyst

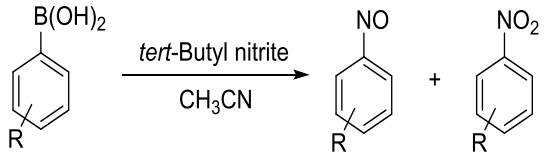

Figure 6. Nitrification of aromatic boric acid by using terbutyl nitrite as the nitrification reagent

In 2012, Maiti et al. [16] reported that the nitrification reaction of aryl boric acid was achieved under the oxidation condition of strong oxidant potassium persulfate with bismuth nitrate as nitrification reagent and toluene as solvent (FIG. 7), and the yield was 35%-100%.The system is also suitable for the conversion of alkene boric acid, and the yield of styrene boric acid as substrate is 48%.In the same year, Vishwakarma and Bharat et al. [17] reported that good yields (70%-90%) could be obtained without the addition of potassium persulfate and catalysts.

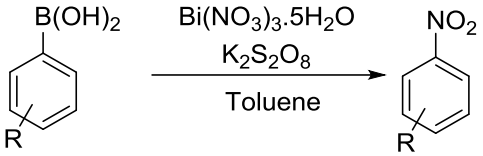

Figure 7. Nitrification of aromatic boric acid by using bismuth nitrate as the nitrification reagent under the oxidation condition of strong oxidant potassium persulfate

In 2013, Al-Masum et al. [18] reported that nitrification of alkene potassium trifluoroborate was achieved using sodium nitrite as nitrification agent and Pd catalyst. However, the effect of this condition on aryl potassium borate was poor (Figure 8). After improvement, better results can be obtained by using bismuth nitrate as nitrification reagent without catalyst [19] (Figure 9), with a yield of 49%-99%.

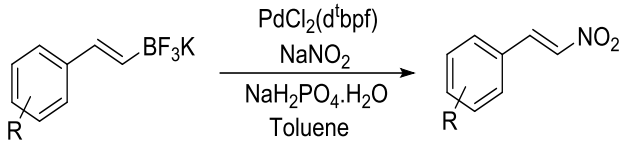

Figure 8. Nitrification of aromatic boric acid by using sodium nitrite as nitrification agent and Pd catalyst

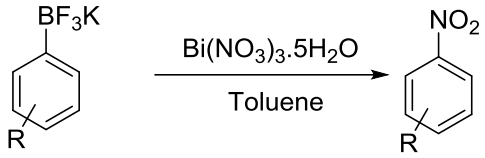

Figure 9. Nitrification of aromatic boric acid by using bismuth nitrate as nitrification reagent without catalyst

In 2013, Yang et al. [20] reported that the nitrification of aromatic boric acid series compounds was realized using ferric nitrate nine hydrate as nitrification agent and toluene as solvent (Figure 10) with a yield of 60%-92%.The obvious difference between this reaction condition and other reported reactions is that the reaction requires nitrogen protection.

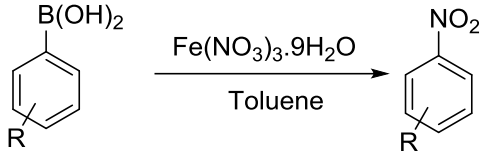

Figure 10. Nitrification of aromatic boric acid by using ferric nitrate nine hydrate as nitrification agent and toluene as solvent

In 2014, Cheon et al. [21] reported that silver nitrate was used as nitrification agent to achieve the quantitative nitrification of dimethylaminobenboric acid or ester (Figure 11).

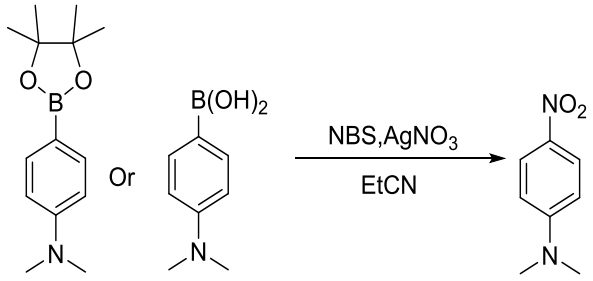

Figure 11. Quantitative nitrification of dimethylaminobenboric acid or ester by using silver nitrate as nitrification agent

In 2015, Goswami et al. [22] reported that the nitrification of aryl boric acid was achieved with sodium nitrite as nitrification agent under the action of NBS and PIFA (Figure 12).Under these conditions, the substrate

was extended and the yield of heterocyclic boric acid and fatty boric acid was good (74%-94%).

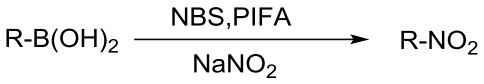

Figure 12. Nitrification of aromatic boric acid by using aryl boric acid as nitrification agent under the action of NBS and PIFA

In 2017, Shen et al. [23] reported that the nitrification of aryl boric acid was achieved using 68% nitric acid aqueous solution and trifluoroacetic acid as nitrification agent (Figure 13), with the yield of 0-95%.The 3,5-difluoro - substituted boric acid basically can't get the product.

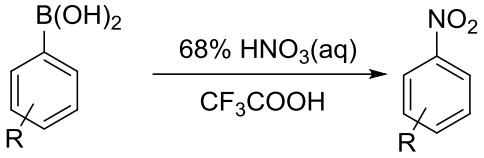

Figure 13. Nitrification of aromatic boric acid by using 68% nitric acid aqueous solution and trifluoroacetic acid as nitrification agent

In 2018, Guo et al. [24] reported that the nitrification of aryl boric acid was achieved with the combination of copper nitrate and trifluoroacetic acid as nitrification agent, and the yield was 51%-96% (Figure 14).

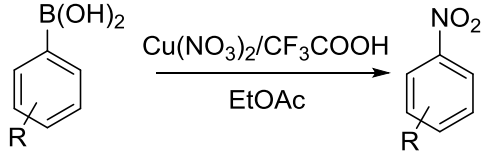

Figure 14. Nitrification of aromatic boric acid by using the combination of copper nitrate and trifluoroacetic acid as nitrification agent

In 2018, Moosvi-Zare and Zolfigol et al. [25] reported that 1, 3-imidazolium disulfonic acid ([DSim]NO_3) was used as the nitrification reagent to achieve the nitrification of aryl boric acid and derivatives.It is worth mentioning that the system can also convert alkene and aryl carboxylic acids to nitrification (Figure 15).

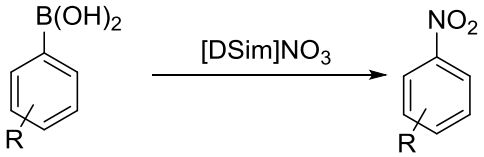

Figure 15. Nitrification of aromatic boric acid by using 1, 3-imidazolium disulfonic acid ([DSim] NO3) as nitrification agent

In 2019, Thakur and Bora et al. [26] reported that the nitrification of boric acid was achieved with zirconium oxygen nitrate hydrate as nitrification agent under the action of I2 (Figure 16), and the yield was 78%-89%.

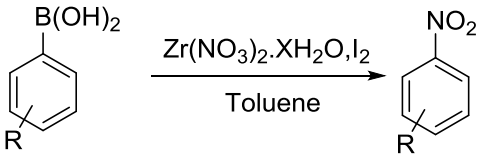

Figure 16. Nitrification of aromatic boric acid by using zirconium oxygen nitrate hydrate as nitrification agent

In 2020, Katayev et al. [27] reported two methods of transforming aryl boric acid into nitro compounds: Photocatalytic nitrification of boric acid using N-nitrosuccinimide as nitrification reagent was first reported. The nitration reaction of boric acid was reported using n-nitrosaccharin as the nitration reagent (Fig. 17).

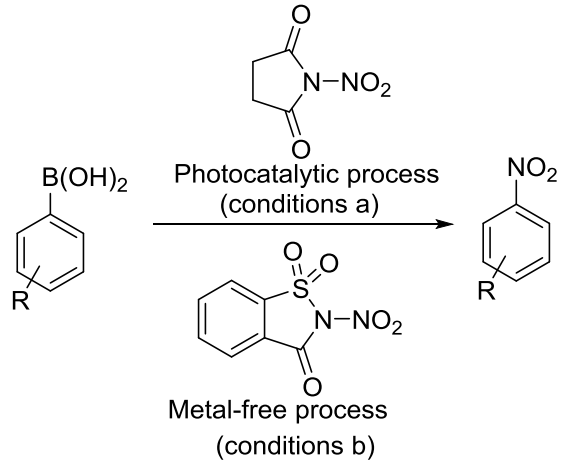

Figure 17. Nitrification of aromatic boric acid by using N-nitrosuccinimide or n-nitrosaccharin as nitrification agent

3. Conclusions and Prospects

In summary, the conversion of boric acid and borate as raw materials to nitro compounds is one of the effective means of nitrification synthesis. From the early yield is not high, selectivity is poor, to visible light catalyzed boric acid to generate nitro compounds. After so many years of development, although much progress has been made, there is still a long way to go to explore moderate, efficient and environmentally friendly catalytic systems and develop more environmentally, economically and socially beneficial synthetic methods.

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