INTRODUCTION

The sulfonylurea herbicides with extremely high effect, low poison, low cost and other characteristics got the extensive expansion application quickly after the development, which was one of the important milestones of the agrochemical development history [1]. Iodosulfuron-methyl (1) was a sulfonylurea postemergence herbicide. Iodosulfuron-methyl-sodium was an active ingredient of the Alister Grande 190 OD herbicide manufactured by Bayer Crop Science, which was registered for use in Poland in 2008. Iodosulfuron-methyl can affect the activity of the acetolactate synthase (ALS) enzyme, leading to plant deformation and death, growth retardation and chlorosis [2-4]. It usually existed in the formation of methyl ester and sodium salt in the application and mainly applied to variety of gramineous weeds and broad-leaved weeds that grow in spring and winter wheat, durum wheat and triticale [5,6]. The herbicide was safe for the cereal crops and has no influence on succeeding crops.

Several syntheses of 2-methoxycarbonyl-5-iodobenzene sulfonamide had been reported in the literature [7]. Diao reported the raw material was not easy to get and high cost [8]. Wang et al. reported to use the hyper-toxic potassium dichromate and iron powder [9]. A large quantity of iron mud pollution was produced in the iron powder reduction. This paper reported a convenient and efficient synthesis of 2-methoxycarbonyl-5-iodobenzene sulfonamide (7) utilizing a non-toxic oxidant potassium permanganate and environment friendly hydrogenation reduction reaction using aluminum-nickel alloy catalyst in good yield. A convenient and most practical approach to the synthesis of 2-methoxycarbonyl-5-iodobenzene sulfonamide (7) involved sulfochlorination, ammoniation, oxidation, reduction and iodination reactions.

EXPERIMENTAL

Reagents and solvents were obtained from commercial suppliers and were used without further purification. All melting points were determined on a XT34 binocular microscope (Beijing Tech Instrument Co., China) and were not corrected.

A convenient and concise synthesis of 2-methyl-5-nitrobenzene sulfonamide can be achieved by sulfochlorination and ammoniation with p-nitrotoluene as raw materials for an 81.2 % yield. 6-Aminosaccharin can be produced via oxidation and reduction in a 64.3 % yield and then the iodination using potassium iodide can afford 6-iodosaccharin with a 70.8 % yield. 2-Methoxycarbonyl-5-iodobenzene sulfonamide can be produced via esterification in a 94.1 % yield.

Keywords: 2-Methyl-5-nitrobenzene sulfonamide, Sulfochlorination, Ammoniation, Oxidation, Iodination, Esterification.
mL) was heated to 50 °C, chlorosulfonic acid (35.4 g, 0.3 mol) was added drop-wise with stirring for over 30 min. The mixture was heated to 60 °C for 6 h. Ice water (500 mL) was added at the end of the reaction with stirring. The aqueous mixture was extracted three times with 1,2-dichloromethane (25 mL, 0.33 mol) was added drop-wise combined the organic layers at 10 °C, the mol) was added drop-wise with stirring for over 30 min. The reaction mixture was concentrated under reduced pressure in the end of the reaction. The crude residue was taken up in water (80 mL) and filtered, washed with water to afford off-white solid 3 (35.1 g, 81.2 % yield), m.p.: 183.2-184.8 °C (lit. [10] m.p.: 183-185 °C) 1H NMR (CDCl3, 300 MHz) δ, ppm: 7.53 (3H, s), 7.24 (2H, s, NH2), 7.55 (1H, d, J = 8.4 Hz), 8.26 (1H, d, J = 8.4 Hz), 8.82 (1H, s).

6-Nitrosaccharin (4): 2-Methyl-5-nitrobenzene sulfonamide (3, 26.1 g, 0.10 mol), benzyl triethyl ammonium chloride (TEBA) (1.2 g, 5.2 mmol) and water (250 mL) were mixed together and heated to 95 °C. The reaction mixture was heated to 95 °C for 8 h. The reaction residue was filtered and washed with hot water (80 mL) twice, the solution was acidified with concentrated hydrochloric acid to pH 2. A white solid was filtered off and recrystallized from ethyl alcohol to give 6-nitrosaccharin (4, 22.8 g, 71.4 % yield), m.p.: 205.5-206.9 °C (lit. [11,12] m.p.: 212-214 °C).

6-Iodosaccharin (6): 6-Aminosaccharin (5), benzyl triethyl ammonium chloride (TEBA) (1.2 g, 5.2 mmol) and water (250 mL) were mixed together and hea ted to 95 °C. The potassium permanganate (15.7 g, 0.1 mmol) was added in batches and then added water (50 mL) finally. The reaction mixture was heated to 95 °C for 8 h. The reaction mixture was heated to 50 °C for 1 h. In the end of reaction, the mixture was cooled to room temperature, filtrated and washed with water, recrystallized from ethyl alcohol to give 6-iodosaccharin (6, 21.9 g, 70.8 % yield), m.p.: 224.6-227.5 °C (lit. [13] m.p.: 224-226 °C). 1H NMR (CDCl3) δ, ppm: 7.73 (d, J = 8.0 Hz, 1H), 8.19 (d, J = 8.0 Hz, 1H), 8.24 (1H, 10.2(1H, br. NH).

2-Methoxycarbonyl-5-iodobenzene sulfonamide (7): 6-Iodosaccharin (6, 31.0 g, 0.10 mol) was dissolved in methanol (200 mL), concentrated sulfuric acid (2 mL) was added drop-wise with stirring, the mixture was heated under reflux for 6 h. The mixture was cooled to room temperature. In the end of reaction, the methanol was removed and the residue was taken up in sodium hydrogen carbonate saturated aqueous (120 mL) to adjust pH 8, filtered and washed with water, recrystallized from methanol to afford 2-methoxycarbonyl-5-iodobenzene sulfonamide (7, 32.1 g, 94.1 % yield), m.p.: 175-179 °C (lit. [14] m.p.: 176-177 °C).

RESULTS AND DISCUSSION

Recently studied using the sulfonyleurea class of herbicides and a key intermediate 2-methoxycarbonyl-5-iodobenzene sulfonamide (7), showed that the efficient synthesis of 6-aminosaccharin (5) with 6-nitrosaccharin (4) in the presence of aluminum-nickel catalyst afforded 2-methoxycarbonyl-5-iodobenzene sulfonamide in very high yields, meantime, the optimization of the synthetic conditions for 6-nitrosaccharin was conducted.

Potassium dichromate is a hyper-toxic oxidant, which had limited use in the world. Generally, non-toxic or environ-
mentally friendly oxidant for manufacture should be used. Although potassium permanganate was lower than potassium dichromate in the performance of oxidation, it was a non-toxic oxidant. Potassium permanganate was selected as an oxidant and it was found that the phase translation catalytic benzyl triethyl ammonium chloride could improve the yield of 6-nitrosaccharin. The yield of oxidation was 71.4%.

The traditional reducing process usually adopts iron powder reduction, which produces the serious pollution of iron mud. The hydrogenation reduction technique was an environmentally friendly process in the chemical industry. The 6-nitrosaccharin was treated with hydrogenation reduction using aluminum-nickel alloy catalyst to give 6-aminosaccharin in 94.1% yield.

Conclusion

We described a convenient efficient synthesis of 2-methoxy-carbonyl-5-iodobenzene sulfonamide (7). This present contribution described the utilization of aluminum-nickel alloy catalyst as an environmentally friendly process for the hydrogenation of 6-nitrosaccharin. A convenient and concise process for the synthesis 2-methoxy-carbonyl-5-iodobenzene sulfonamide had been proven to be practical. The current method presented a very promising synthetic process for 2-methoxy-carbonyl-5-iodobenzene sulfonamide because of the following advantages:

• Non-toxic potassium permanganate to replace toxic oxidant sodium dichromate.
• Aluminum-nickel alloy catalytic replaced iron reduction which controlled pollution source from raw material.
• The clean process reported in this paper can be easily developed into larger-scale preparation of 2-methoxy-carbonyl-5-iodobenzene sulfonamide for new sulfonylurea herbicides development.

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REFERENCES