



Catalytic Hydrogenation and Reduction of 4-(2,2,2-Trifluoroethoxy)nitrobenzene

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4-(2,2,2-Trifluoroethoxy)nitrobenzene was used as raw material to create a reaction for 1 h at 70 °C by using ethanol and palladium carbon as solvent and catalyst, respectively, to obtain the desired product 4-(2,2,2-trifluoroethoxy)aniline with 97 % yield and 99.9 % purity. NMR, IR, MS, GC and other analysis and detection methods were used to conduct qualitative and quantitative analyses of the desired product. This paper discussed the process conditions of hydrogenation and reduction reaction and mainly investigated the impact of dosage and recycling of catalyst.

Keywords: 4-(2,2,2-Trifluoroethoxy)aniline, Palladium carbon, Catalytic hydrogenation, Recycling of catalyst.

INTRODUCTION

As an important intermediate, trifluoroethoxy aniline is extensively applied in the field of medicine; it is also used in pesticides and dyestuff, among other applications. Combined 1,3-diamino-4-(2,2,2-trifluoroethoxy)benzene and salt is used as hair dye-because of its advantages, such as better chromaticity, rapid dyeing and nontoxicity¹.

Nitro reduction is currently used in different industrial applications, such as reduction of metals in acid, neutral and alkaline systems; reduction of reductive compound; electro-chemical reduction and catalytic hydrogenation reduction². However, the first three methods cause environmental pollution and are inefficient and complicated. Catalytic hydrogenation reduction is characterized by a clean process, mild reaction conditions, convenient post-treatment and high yield. Catalytic hydrogenation is used in both laboratory research and industrial production. Given the advantages of this process, the present experiment adopted catalytic hydrogenation. The specific synthetic route is as Fig. 1.

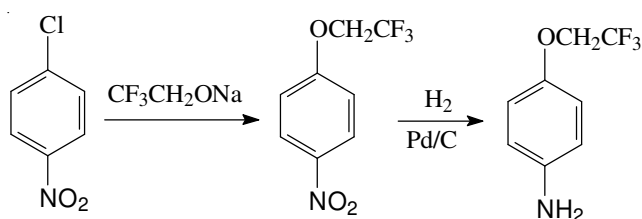


Fig. 1. Synthetic route of 1,3-diamino-4-(2,2,2-trifluoroethoxy)benzene

EXPERIMENTAL

The following equipment were used in this experiment: Yansco micro melting point apparatus (uncalibrated thermometer); Bruker Avance DPX 300 MHz nuclear magnetic resonance spectrometer; TSQ Quantum Ultra Am high-resolution mass spectrometer from Finnigan Corporation; and Nexus 870 FTIR infrared spectrometer from US Nicolet Corporation. 4-Chloronitrobenzene and sodium hydride are chemically pure reagents; ethanol, acetic ether and petroleum ether are analytic reagents; and trifluoroethanol, palladium carbon and hydrogen are industrial products.

Synthesis of 4-(2,2,2-trifluoroethoxy)nitrobenzene: First, 2.4 g (0.1 mol) of sodium hydride and 120 mL of N,N-dimethyl formamide were added into a dried four-neck 250 mL flask. Then, 10 g (0.1 mol) trifluoroethanol was dropped slowly into the flask under the protection of nitrogen ice. The mixture was stirred for about 0.5 h and clear and transparent liquid was obtained. Afterward, 7.88 g (0.05 mol) 4-chloronitrobenzene was added and the temperature was slowly increased to 100 °C to generate a reaction for 3 h. After 2/3 of the solvent was removed through decompression, the mixture was naturally cooled to room temperature. Diluted hydrochloric acid was used to adjust the pH to a slightly acidic value. The mixture was then stored at room temperature. Yellow crystals gradually appeared overnight. Solids were extracted and filtered. After recrystallization with ethanol (95 %), white solids were obtained, with a yield of 98 %, m.p. 69 to 71 °C (value from the literature³: 75.5 to 76.5 °C); MS m/z (%), 220.9 (M^+ , 100), 191.0, 156.0.

Synthesis of 4-(2,2,2-trifluoroethoxy)aniline: First, 11.05 g (0.05 mol) 4-(2,2,2-trifluoroethoxy)nitrobenzene, 150 mL ethanol and 0.3 g palladium carbon were added to a 500 mL autoclave. Hydrogen was injected into the autoclave to increase the pressure to 0.5 Mpa and then the reaction was generated for 1 h at 75 °C. Once the pressure stopped falling, it was maintained for 0.5 h. After the reaction, the mixture was filtered and the filtered liquid was distilled to remove solvent ethanol. Fractions with a temperature range of 140 to 158 °C were collected to create recrystallized V(petroleum ether): V(ethyl acetate) = 10:1. White flaky crystals were obtained with a yield of 97 %, m.p. 66 °C to 68 °C. ¹H NMR (CDCl₃, δ): δ6.80-6.83 (d, 2H, Ar-H), 6.65-6.69 (d, 2H, Ar-H), 2.90 (s, 2H, -NH₂), 4.29 (m, 2H, OCH₂CF₃); IR (KBr, ν_{max}, cm⁻¹): 3462(m), 1504(s), 1258(s), 1202(s), 753(s). MS *m/z* (%), 192.1(M), 163.0, 109.0, 107.9.

RESULTS AND DISCUSSION

Process conditions of hydrogenation reduction

Selecting hydrogenation reduction solvent: 4-(2,2,2-Trifluoroethoxy)nitrobenzene reduction is a heterogeneous catalytic reaction in which the solvent has an important function. Solvent polarity has different effects on the catalytic hydrogenation rate and catalyst selection. These different effects are mainly due to the fact that the solvent changes the catalytic activity and the adsorption of unsaturated substrate, which in turn changes hydrogen adsorption^{4,5}.

Liquid phase catalytic hydrogenation uses inert solvents that are stable to hydrogen, such as water, methanol, ethanol, isopropyl alcohol, ethyl acetate and tetrahydrofuran. Table-1 shows the polarities and boiling points of these solvents.

Ethanol (b.p. 79 °C) (which is higher than the reaction temperature) and proper polarity can better dissolve products. Ethanol is miscible with water, which ensures that catalyst poisoning can be avoided. Water generated from oxide reduction causes aggregation of metal particles, decreasing catalytic activity. In addition, ethanol is nontoxic and easily recyclable. Therefore, it was selected as the solvent.

Temperature for hydrogenation reduction: Hydrogenation is an exothermic reaction. An excessively high temperature will promote side reactions, which will affect product conversion rate. Therefore, a lower temperature should be used to ensure that the proper reaction can be obtained. The hydrogenation temperature of the reaction in this experiment is 70 °C.

Pressure for hydrogenation reduction: Increasing pressure can accelerate reaction speed. However, excessive pressure will cause an unusually severe reaction. Increased heat will negatively affect the reaction equipment and impede safe operation. Therefore, a lower temperature should be used to ensure that the pressure is suitable for the reaction. The recommended hydrogen pressure is 0.5 MPa.

Catalyst

Effect of catalyst dosage on the reaction: One hundred fifty milliliters of ethanol were added to 11.05 g (0.05 mol) 4-(2,2,2-trifluoroethoxy)nitrobenzene. Palladium carbon with a load of 5% was used as catalyst and H₂ pressure was 0.5 Mpa. The reaction was maintained at 70 °C until the pressure in the autoclave increased. In this experiment, the amount of the catalyst was changed to examine the effect of catalyst dosage on the reaction. The results are shown as Table-2.

TABLE-2
IMPACT OF CATALYST DOSAGE ON THE REACTION

The amount of palladium carbon (relative to mass ratio of raw materials)	1 %	3 %	4 %	5 %
Hydrogenation time/min	120	60	50	40
Yield (%)	97.1	97.5	98.1	97.6

The above table indicates that the reaction became faster and hydrogenation time decreased with the increase of the amount of palladium carbon. However, when the amount of palladium carbon was increased to a certain degree, the yield remained at a certain level. When the feeding amount of palladium carbon was 5 %, the reaction speed was rapid and strongly exothermic. Moreover, the yield increased. Therefore, a feeding amount of 3 % is suitable.

Impact of catalyst recycling on the reaction: Catalyst loss occurs during recycling, thereby affecting the reaction speed. In this paper, catalyst recycling was analyzed and studied and an experiment on the process was conducted. The reaction conditions are discussed earlier and the amount of catalyst was 3 % (Table-3).

TABLE-3
IMPACT OF PALLADIUM CARBON RECYCLING ON THE REACTION

Catalyst recycling times	1	2	3	4	5
Yield (%)	97.0	93.9	91.7	84.9	82.5

The above results indicate that as catalyst recycling increased, hydrogenation speed decreased markedly. When catalyst recycling occurred more than three times, the yield decreased to 90 % and below. This decrease is due to various reasons. First, catalyst loss occurred during the recycling process. Second, foreign matters were adsorbed on the activated carbon carrier during the reaction. As a result, the carrier was partially inactivated. To ensure a stable reaction, a small amount of fresh catalyst should be added when the catalyst has been used more than three times.

Catalyst recycling: Recycling of precious metal catalysts, particularly those in liquid phase hydrogenation, is a key issue in precious metal catalysis. The recycling process for waste palladium carbon involves the following steps: treatment of activated carbon, burning of waste catalysts, dissolving of palladium and preparation of new catalysts, among others⁶.

TABLE-1
POLARITIES AND BOILING POINTS OF SOLVENTS

Solvents	Water	Methanol	Ethanol	Isopropyl alcohol	Ethyl acetate	Tetrahydrofuran
Polarities (25 °C)	10.2	6.6	4.3	4.3	4.3	4.2
Boiling points (°C)	100	65	79	82	77	66

The results verified that the palladium carbon catalysts obtained by using the method presented in this paper are as efficient as fresh catalysts.

Conclusions

- 4-(2,2,2-Trifluoroethoxy)nitrobenzene can be used as raw material to obtain 4-(2,2,2-trifluoroethoxy)aniline through palladium carbon catalytic hydrogenation with 97 % yield and 99.9 % purity.

- Catalytic hydrogenation reduction is conducted with the use of ethanol as reactive solvent under a reactive temperature of 70 °C and reactive pressure of 0.5 Mpa.

- In this experiment, the suitable amount of catalyst is 3 %. When the catalyst has been used more than three times, the yield decrease to 90 % and below. Therefore, when the

catalyst has been used more than three times, a small amount of fresh catalyst should be added. Palladium carbon catalysts obtained through recycling are as efficient as fresh catalysts.

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