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One-pot Synthesis of 2,4,5-Trinitroimidazole

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Abstract: An improved one-pot method for the preparation of 2,4,5-trinitroimidazole from 4-nitroimidazole was reported. Its structure was identified by ^{1}H NMR, IR, MS and elemental analysis. The reaction time, reaction temperature and the molar ratio of the reagents of the synthetic route were optimized. Results show that the yield of 2,4,5-trinitroimidazole can reach up to 80.6% under the conditions of reaction time 4 h, reaction temperature 120 ℃ and the molar ratio of n (4-nitroimidazole) : n(65% HNO_3) : n(AcOH) = 1 : 30 : 30.

Key words: organic chemistry; one-pot synthesis; 4-nitroimidazole; nitration; 2,4,5-trinitroimidazole

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1 Introduction

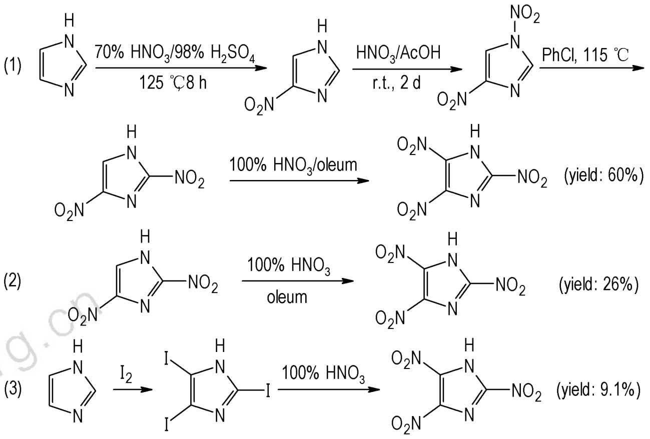
During the past decades, considerable efforts have been focused on the development of nitrogen-rich high energy density materials (HEDMs) with high performance and low sensitivity as well as environmental compatibility[1-4]. Imidazole derivatives with multi-nitro groups are expected to be the typical energetic compounds as members of HEDM with excellent energetic properties and low sensitivity[5-7]. For instance, it was reported that 2,4,5-trinitroimidazole had similar energetic properties (density, 1.93 g·cm^{-1}; detonation velocity, 8.73 km·s^{-1}; detonation pressure, 32.1 GPa; impact sensitivity, 68 cm)[8] with hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX, density, 1.82 g·cm^{-1}; detonation velocity, 8.70 km·s^{-1}; detonation pressure, 34.0 GPa; impact sensitivity, 28 cm)[9] and had been widely used both in military and civilian applications. Therefore, it is not surprising that research on the synthesis of 2,4,5-trinitroimidazole has received significant attention[10]. Upon now, the main synthesis routes were reported using imidazol[11], 2,4,5-triiodoimidazol[12] or 2,4-dinitroimidazole as the starting material[13], which have disadvantages like toxicity, high cost, low yield (Scheme 1, 60%, 26% and 9.1%, respectively) and tedious synthetic steps.

Therefore, we improved the synthesis of 2,4,5-trinitroimidazole using commercially available starting materials (4-nitroimidazole), and by an improved one-pot procedure with better yield, which can avoid toxic, decrease cost, and is favor in scaled-up preparation.

2 Experimental

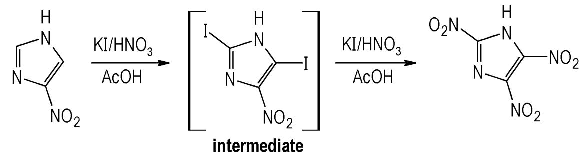
2.1 Reagent and instrument

All chemicals were analytical grade obtained commercially and used as received. ^{1}HNMR spectra were recorded on a Bruker 500 MHz nuclear magnetic resonance spectrometer operating at 500 MHz using the DMSO-d_6 as the locking solvent. The chemical shifts are reported relative to tetramethylsilane for the ^{1}H NMR spectra. IR spectra were recorded by using KBr pellets on a Thermo Nicolet IS10 IR instrument. ESI-MS were recorded on a Finnigan TSQ Quantum ultra AM mass spectrometer. Elemental analyses were recorded by a Vario EL III elemental analyser (Germany).



Scheme 1 Previous synthesis of 2,4,5-trinitroimidazole

2.2 Synthetic route



Scheme 2 One-pot synthesis of 2,4,5-trinitroimidazole

2.3 Synthesis of 2,4,5-trinitroimidazole

To a vigorous stirred solution of 4-nitroimidazole (1.13 g,

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10 mmol) in a mixture of 65% nitro acid (17.5 mL) and acetic acid (15 mL) was added KI (3.32 g, 20 mmol) in portions at 0 ℃. The resulting mixture was gradually warmed up to room temperature and stirred for 30 min. Then the system was heated at 120 ℃ for 4 h. After cooling to room temperature, the reaction mixture was poured on 200 g ice. The separated precipitate was filtered off and the filtrate was extracted with ethyl acetate (5×60 mL). The combined organic layer were washed with ice water (3×10 mL), dried by anhydrous sodium sulfate, filtered, and then concentrated under reduced pressure. Recrystallized from ethyl acetate and 2,4,5-trinitroimidazole was obtained as slightly colored crystals, yield: 1.64 g (80.6 %). ^{1}H NMR (500 MHz, DMSO-d_6,) δ: 7.08 (s, H); IR (KBr, ν/cm^{-1}): 3417, 3131, 2170, 1641, 1538, 1470, 1402, 1322, 1296, 1210, 1156, 1109, 1049, 869, 813, 754, 634, 576; ESI-MS (*m/z*): 202 [M−H]$^-$; elemental analysis calcd for $C_3HN_5O_6$ (%): C 17.73, H 0.49, N 34.48; found: C 17.86, H 0.43, N 34.61.

3 Results and discussion

3.1 The optimization of the reaction conditions

As was shown in Scheme 2, the synthesis started from the commercially obtained 4-nitroimidazole and then nitrified by the 65% HNO_3/KI/AcOH system. The reaction time, reaction temperature and the molar ratio of the reagents as the key parameters of the reaction were investigated and optimized. During the procedure, 4-nitro-2,5-diiodoimidazol was detected as the intermediate and thus the molar ratio 1 : 2 of 4-nitroimidazole and KI was selected. Correlations between yields and reaction time, reaction temperature and the molar ratio of 4-nitroimidazole and 65% HNO_3/AcOH were investigated as follows.

3.1.1 Effect of reaction time on yield

Under the conditions of reaction temperature 120 ℃, *n*(4-nitroimidazole) : *n*(65% HNO_3) : *n*(AcOH)=1 : 30 : 30, the correlation between yield and reaction time was investigated and summarized in Fig. 1. From Fig. 1, it is clear that the yield of 2,4,5-trinitroimidazole increases as the reaction time prolonged and there is a maximum (80.6%) when the reaction time is 4 h. With the continuing prolongation of reaction time, the yield became to decrease slightly which may be due to the by-products.

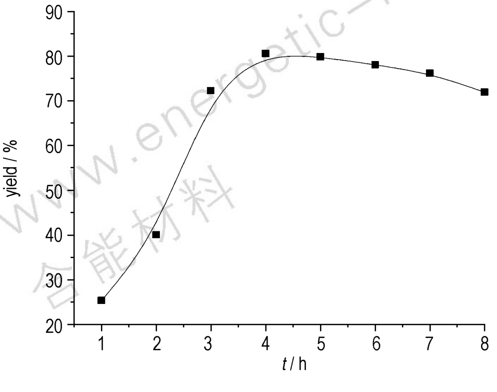

Fig. 1 Effect of reaction time on the yield

3.1.2 Effect of reaction temprature on yield

Under the conditions of reaction time 4 h, molar ratio of *n*(4-nitroimidazole) : *n*(65% HNO_3) : *n*(AcOH)=1 : 30 : 30, the ralationship between yield and reaction temperature was investigated and summarized in Fig. 2. From Fig. 2, it is clear that the yield of 2,4,5-trinitroimidazole increases as the reaction temperature increases and there is a maximum when the reaction temperature is 120 ℃. With the continuing improvement of the reaction temperature, the yield became to decrease sharply. This may be caused by the side reactions or the 2,4,5-trinitroimidazole decomposition yielding any other by-products when the temperature was above 120 ℃.

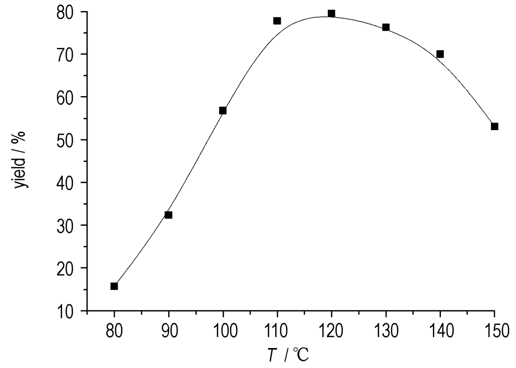

Fig. 2 Effect of reaction temperature on the yield

3.1.3 Effect of molar ratio of the reagents on yield

Under the conditions of reaction time 4 h, reaction temperature 120 ℃, the correlation between yield and molar ratio of 4-nitroimidazole and 65% HNO_3/AcOH was investigated and summarized in Fig. 3. It is found that the yield of 2,4,5-trinitroimidazole increases as the molar ratio of 4-dinitroimidazole and 65% HNO_3/AcOH increases to the maximum when *n*(4-nitroimidazole) : *n*(65% HNO_3) : *n*(AcOH) = 1 : 30 : 30. With the continuing increase of the molar ratio, no improvement of the yield was observed, which indicates that it has reached a chemical equilibrium at this point.

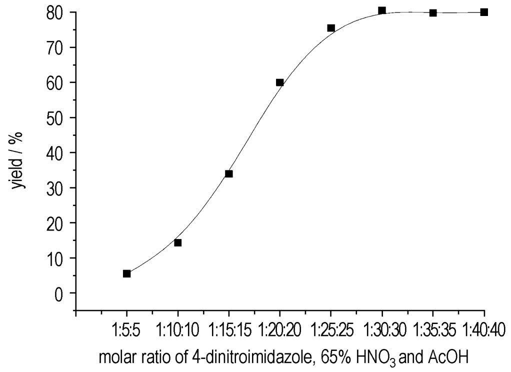

Fig. 3 Effect of the molar ratio of the reagents on the yield

Results indicates that the reaction temperature is the most significant impact factor in the reaction and the optimized conditions of the reaction are as follows: reaction time 4 h, reaction temperature 120 ℃, and the molar ratio of *n*(4-nitroimidazole) : n(65% HNO_3) : n(AcOH) = 1 : 30 : 30. The yield of 2,4,5-trinitroimidazole can reach up to 80.6% which is better than the reference reported[11-13].

3.2 Highlights

This method is less cost, less toxic, higher yield, and better safety compared with the reference [11-13]. For instance, we avoid to use 2,4,5-triiodoimidazol as the starting material, which is obtained by the reaction of imidazole and iodine with an expensive and toxic procedure. No other organic solvent (e.g. PhCl) was used in the reaction to avoid solvent loss; 2,4-dinitroimidazole was not selected as the starting material since it is a high energy density material itself and it may be dangerous in the scaled-up preparation of 2,4,5-trinitroimidazole. Moreover, strong acid such as 100% nitric acid and oleum are also absence of the reaction to avoid contamination.

4 Conclusion

An improvement of one-pot the synthesis of 2,4,5-trinitroimidazole was reported with yield of 80.6%, which is efficient, simple and eco-friendly. The optinal condition was obtained as follows the reaction time 4 h, reaction temperature 120 ℃ and the molar ratio of n(4-nitroimidazole) : n(65% HNO_3) : n(AcOH) = 1 : 30 : 30.

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一锅法合成2,4,5-三硝基咪唑

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摘　要: 以4-硝基咪唑为原料, 用 HNO_3/KI/AcOH 作为硝化体系,通过一锅法制备了2,4,5-三硝基咪唑,用^{1}H NMR, IR, MS 以及元素分析对其结构进行了表征。优化了反应路线,结果表明,在反应时间4 h,反应温度为120 ℃,n(4-硝基咪唑) : n(65% HNO_3) : n(AcOH) = 1 : 30 : 30 条件下,目标化合物产率高达80.6%。

关键词: 有机化学; 一锅法合成; 4-硝基咪唑; 硝化; 2,4,5-三硝基咪唑

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